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(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: SHOWELL, Michael, Stanford [US/US]; 685 Compton Road, Cincinnati, OH 45231 (US). ZHU, Yong [CN/US]; 4348 Bromyard Avenue, Cincinnati, OH 45241 (US). WELLS, Eric [US/US]; 1440 W. Kemper Road #1601, Cincinnati, OH 45240 (US). MOESE, Rosa, Laura [US/US]; 8815 Eagle Creek Court, West Chester, OH 45069 (US). BETTIOL, Jean–Luc, Philippe [FR/BE]; 93, avenue Slegers, B–1200 Brussels (BE). BUSCH, Alfred [DE/BE]; Handelsstraat 210, B–1840 Londerzeel (BE). YOSHIKAWA, Aki [JP/JP]; 3–6–23, Sumiyoshi miyamachi, Higashinada–ku, Kobe 658–0053 (JP). BECHMANN, Georg [DE/BE]; Clos–St. Georges 5, B–1970 Wezembeek–Oppem (BE).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217–1087 (US).

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(54) Title: DETERGENT COMPOSITIONS COMPRISING AN ENZYME SYSTEM

(57) Abstract

The present invention relates to detergent compositions comprising a mannanase, a pectate lyase and a xyloglucanase providing superior stain removal, dingy cleaning and whiteness maintenance.

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DETERGENT COMPOSITIONS COMPRISING AN ENZYME SYSTEM

Field of the Invention

The present invention relates to detergent compositions comprising an enzymatic system comprising a mannanase, a xyloglucanase and a pectate lyase.

Background of the invention

Performance of a detergent product is judged by a number of factors, including the ability to remove soils, and the ability to prevent the redeposition of the soils, or the breakdown products of the soils on the articles in the wash Therefore, detergent compositions include nowadays a complex combination of active ingredients which fulfil certain specific needs. In particular, current detergent formulations generally include surfactants and detergent enzymes providing cleaning and fabric care benefits.

Removal of stains stemming from plants, wood, mould-clay based soil, muddy soils, and fruits is one of today's toughest cleaning tasks; especially with the trend toward low wash temperatures. These stains typically contain complex mixtures of fibrous material based mainly on carbohydrates and their derivatives : fibres and cell wall components. Plant based soils are additionally accompanied with amylose, sugars and their derivatives. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils. Indeed, pectin polymers are important constituents of plant cell walls. Pectin is a hetero-polysaccharide with a backbone composed of alternating homogalacturonan (smooth regions) and rhamnogalacturonan (hairy regions). The smooth regions are linear polymers of 1,4-linked alpha-D-galacturonic acid. The galacturonic acid residues can be methyl-esterified on the carboxyl group to a varying degree, usually in a non-random fashion with blocks of polygalacturonic acid being completely methyl-esterified. The substrates on which pectin containing stains are commonly found can be fabrics, dishware or hard surfaces.

In addition, the complex nature of everyday "body" soils typically found on pillow cases, T-shirts, collars and socks, provides a continuous thorough cleaning challenge for detergents. These soils are difficult to remove completely due in part to their interaction with the pectin components in the primary cell walls of cotton fibers comprising cotton containing fabrics, and often residues build up on such fabric leading to dinginess and yellowing. Moreover, body fluid stains, such as blood and menstrual fluids, are often difficult to remove effectively from a soiled item, especially when the stains have been aged. Everyday body soils are also found on sanitary and kitchen surfaces such as bathtubs, toilet bowls and dishware.

The use of enzymes in detergents is well-known in the art. For example, amylase enzymes have long been recognised in detergent compositions to provide the removal of starchy food residues or starchy films from dishware or hard surfaces or to provide cleaning performance on starchy soils as well as other soils typically encountered in laundry applications. Protease enzymes have long been recognised in detergent compositions to provide the removal of proteinaceous food residues from dishware, hard surfaces or to provide cleaning performance on proteinaceous soils as well as other soils typically encountered in laundry applications. Additionally, the use of cellulase is also well-known in the art. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and generally improved handfeel characteristics to the fabric structure. The inclusion of lipolytic enzyme (e.g. lipase) in detergent compositions for improved cleaning performance is known, e.g. enhancement of removal of triglycerides containing soils and stains from fabrics.

Pectin degrading enzymes are known to provide soil/stain removal benefits when used in washing and cleaning operations, specifically to provide the removal of a broad range of plant and fruit based stains and enhance the realistic item cleaning profile of the detergent compositions. Indeed, removal of stains stemming from plants, wood, mould-clay based soil and fruits is one of today's toughest cleaning task; in particular with the trends to move to low wash temperatures. Food soils are often difficult to remove effectively from a soiled substrate. Highly coloured or "dried-on" soils derived from fruit and/or vegetable juices are particularly challenging to remove. Specific examples of such soils would include orange juice, tomato juice, banana, mango or broccoli soils.

Xyloglucan specific endoglucanases having a high xyloglucan-degrading activity may be of particular use for degradations of cell wall material having a high xyloglucan content, for instance in the wine and fruit industries, for pectin extraction and for removal of hemicelluloses from textile fibers. Furthermore it

has been recognised that such specific xyloglucan enzymes removes the xyloglucan without altering the cellulose. The use of such xyloglucan specific endoglucanases in detergent compositions has only been recently discovered as described in the co-pending international patent application PCT/US98/09126, internationally filed by Procter and Gamble on May 5, 1998.

Another class of enzymes that have been recently applied in the detergent industry is mannanase. Mannanase enzymes are known for their hydrolytic activity on mannans-containing stains/soils such as food and/or cosmetic stains/soils. Food and cosmetic stains/soils represent an imporatnt part of consumer relevant stains/soils and often comprise additives such as thickener / stabiliser agents. Indeed, hydrocolloids gums and emulsifiers are commonly used additives.

There is a continuous effort in the detergent industry to formulate detergent compositions which provide superior cleaning performance. This objective has been met by formulating detergent compositions comprising a specific enzyme system comprising a mannanase, a pectate lyase and/or a xyloglucanase.

It has been surprisingly found that the combined use of the following three specific enzymes : a mannanase, a pectate lyase and a xyloglucanase, provides superior cleaning due to the synergistic effect of the mixed enzyme system, i e superior stain removal, dingy cleaning and whiteness maintenance. Specifically, it has been found that the combined use of said enzymes provides outstanding stain removal on key stains, even at very low wash temperature and/or low detergent level, in laundry, dishwashing and hard surface cleaning applications

It has been further found that the performance of the detergent compositions of the present invention is enhanced by the addition of selected surfactants, a builder, another enzyme and/or a bleach system.

Mannanases have been identified in several *Bacillus* organisms. For example, Talbot et al., Appl. Environ. Microbiol., vol. 56, No. 11, pp. 3505-3510 (1990) describes a β-mannanase derived from *Bacillus stearothermophilus* in dimer form having a MW of 162 kDa and an optimum pH of 5.5-7.5. Mendoza et al., World J. Micobio. Boitech., vol. 10, no. 5, pp. 551-555 (1994) describes a β-mannanase derived from *Bacillus subtilisis* having a MW of 38 kDa, an optimum activity at pH 5.0 / 55°C and a pI of 4.8. J0304706 discloses a β-mannanase derived from *Bacillus sp.* having a MW of 37+/- 3kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. J63056289 describes the production of an alkaline, thermostable β-mannase, which hydrolyses β-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno:oligo:saccharides. J63036774 relates to a *Bacillus* micro-organism FERM P-8856 which produces β-mannanase and β-mannosidase, at an alkaline pH. A purified mannanase from *Bacillus amyloliquefaciens* and its method of preparation useful in the bleaching of pulp and paper, is disclosed in WO97/11164. WO91/18974 describes an hemicellulase such as a glucanase, xylanase or mannanase, active at extreme pH and temperature and the production thereof. WO94/25576 describes an enzyme exhibiting a mannanase activity derived from *Aspergillus aculeatus* CBS 101.43, that might be used for various purposes for which degradation or modification of plant or algae cell wall material is desired. WO93/24622 discloses a mannanase isolated from *Trichoderma reesie* for bleaching lignocellulosic pulps.

Pectin degrading enzymes as detergent enzymes are described in EP-A-751 990 and in co-pending patent applications PCT/US96/12963, PCT/US96/12962. PCT/US96/12959, PCT/US96/12960 and PCT/US96/12691; all filed on August 09, 1996. WO95/35362 discloses cleaning compositions containing plant cell wall degrading enzymes having a pectinase and/or hemicellulase and optionally cellulase activity for the removal of stains from vegetable origin.

Xyloglucan specific endoglucanases have been identified in various plants, see for example, the disclosure of Fry et al., Biochem. J. (1992), Vol. 282, pp 821-828, Nishitani and Tominaga, The Journal of Biol. Chemistry (1992). Vol. 267, No. 29, pp. 21058-21064, Hayashi et al., Plant Physiol., (1984), Vol. 75, pp. 605-610, McDougall and Fry, J. Plant Physiol., (1991), Vol. 137, pp. 332-336, and WO 93/17101. All of these enzymes have been found to have transferase activity (as defined e.g. by Fry et al., 1992 and Nishitani et al., 1992) and are therefore said not to be classified as a real endoglucanase. Further, a xyloglucan specific endoglucanases in microorganisms is described in WO 94/14953. Therein, it is generally stated that "endoglucanases having a high xyloglucan-degrading activity may be of particular use for degradations of cell wall material having a high xyloglucan content, for instance in the wine and fruit industry, for pectin-extraction and for removal of hemicelluloses from textile fibres". Specifically referred to for this last property is the use of these enzymes to manufacture textile fibers: "The hemicellulose like xyloglucan has to be removed from plant fibers like cotton, flax, hemp and jute before these can be used for textiles. For this purpose endoglucanase of type II [i.e., the xyloglucan-specific enzymes] has the advantage that it specifically removes the xyloglucan without damaging the cellulose." "Furthermore, the endoglucanases of the invention and analogous thereof may be used to treat cellulose fibres or cellulose-fibre rich material. The endoglucanases may e.g. be used in the paper industry to improve the drainage of pulp, and to treat fabrics such as cotton fabrics, to give a more smooth fabric."

However, the synergistic combination of a mannanase, a pectate lyase and a xyloglucanase, for superior cleaning performance in a detergent composition, i.e superior stain removal, dingy cleaning and whiteness maintenance, has never been previously recognised.

Summary of the invention

The present invention relates to detergent compositions, including laundry, dishwashing, hard surface cleaner compositions, comprising a mannanase, a pectate lyase and a xyloglucanase, for superior cleaning performance, i.e. superior stain removal, dingy cleaning and whiteness maintenance.

Detailed description of the invention

The detergent compositions of the present invention comprise as essential elements a mannanase, a pectate lyase and a xyloglucanase. It has been surprisingly found that such compositions provide superior cleaning performance, i.e. superior stain removal, dingy cleaning and whiteness maintenance.

Not wishing to be bound by theory it is believed that the combination of all three enzymes, Mannanase, Pectate Lyase and Xyloglucanase, is more effective at breaking down complex carbohydrate soils/stains than the individual enzymes alone. Many vegetable and fruit-based stains contain intact plant cell wall material which is comprised of pectins and xyloglucans. In addition, hydrocolloid gums, such as guar gum, are commonly used stabilizers and rheology modifiers in prepared foods. Thus, it is expected that in vegetable and/or fruit-based food soils/stains, pectin, xyloglucan and mannan substrates are to be found. The polymeric, branched nature of these substrates is believed to attract and hold stain/soil components to fabric, dish, and/or hard surfaces. Attacking these substrates with said specific mixture of enzymes provides overall superior removal of soils/stains, especially food-based soils and stains, than is otherwise obtained with the individual enzyme alone. In addition, it is known that cotton fibers retain some portion of the primary cell wall. The pectins and xyloglucans

present in this residual primary cell wall layer present a preferred binding site for the hydrocolloid gums found in a number of prepared foods and personal and beauty care products such as shampoos, body lotions, and make-up. When such materials contact cotton fabrics they are difficult to remove with standard detergents. It is proposed that the enzyme mixture contemplated in this invention is effective at removing such stains because the Pectate Lyase and Xyloglucanase aid in removal of the residual primary cell wall components of the cotton garment while the Mannanase serves to break down the hydrocolloid gums found in the soils/stains themselves.

The Mannanase Enzyme

The first essential element of the detergent compositions of the present invention is a mannanase enzyme.

Encompassed in the present invention are the following three mannans-degrading enzymes : EC 3.2.1.25 : β-mannosidase, EC 3.2.1.78 : Endo-1,4-β-mannosidase, referred therein after as "mannanase" and EC 3.2.1.100 : 1,4-β-mannobiosidase (IUPAC Classification- Enzyme nomenclature, 1992 ISBN 0-12-227165-3 Academic Press).

More preferably, the detergent compositions of the present invention comprise a β-1,4-Mannosidase (E.C. 3.2.1.78) referred to as Mannanase. The term "mannanase" or "galactomannanase" denotes a mannanase enzyme defined according to the art as officially being named mannan endo-1,4-beta-mannosidase and having the alternative names beta-mannanase and endo-1,4-mannanase and catalysing the reaction: random hydrolysis of 1,4-beta-D-mannosidic linkages in mannans, galactomannans, glucomannans, and galactoglucomannans.

In particular, Mannanases (EC 3.2.1.78) constitute a group of polysaccharases which degrade mannans and denote enzymes which are capable of cleaving

polyose chains contaning mannose units, i.e. are capable of cleaving glycosidic bonds in mannans, glucomannans, galactomannans and galactogluco-mannans. Mannans are polysaccharides having a backbone composed of β-1,4- linked mannose; glucomannans are polysaccharides having a backbone or more or less regularly alternating β-1,4 linked mannose and glucose; galactomannans and galactoglucomannans are mannans and glucomannans with α-1,6 linked galactose sidebranches. These compounds may be acetylated.

The degradation of galactomannans and galactoglucomannans is facilitated by full or partial removal of the galactose sidebranches. Further the degradation of the acetylated mannans, glucomannans, galactomannans and galactogluco-mannans is facilitated by full or partial deacetylation. Acetyl groups can be removed by alkali or by mannan acetylesterases. The oligomers which are released from the mannanases or by a combination of mannanases and α-galactosidase and/or mannan acetyl esterases can be further degraded to release free maltose by β-mannosidase and/or β-glucosidase.

Mannanases have been identified in several *Bacillus* organisms. For example. Talbot et al., Appl. Environ. Microbiol., Vol.56, No. 11, pp. 3505-3510 (1990) describes a beta-mannanase derived from *Bacillus stearothermophilus* in dimer form having molecular weight of 162 kDa and an optimum pH of 5.5-7.5 Mendoza et al., World J. Microbiol. Biotech., Vol. 10, No. 5, pp. 551-555 (1994) describes a beta-mannanase derived from *Bacillus subtilis* having a molecular weight of 38 kDa, an optimum activity at pH 5.0 and 55C and a pI of 4.8. JP 03047076 discloses a beta-mannanase derived from *Bacillus* sp., having a molecular weight of 373 kDa measured by gel filtration, an optimum pH of 8-10 and a pI of 5.3-5.4. JP-63056289 describes the production of an alkaline thermostable beta-mannanase which hydrolyses beta-1,4-D-mannopyranoside bonds of e.g. mannans and produces manno-oligosaccharides. JP-63036774 relates to the *Bacillus* microorganism FERM P-8856 which produces beta mannanase and beta-mannosidase at an alkaline pH. JP-08051975 discloses alkaline beta-mannanases from alkalophilic *Bacillus* sp. AM-001. A purified

mannanase from *Bacillus amyloliquefaciens* useful in the bleaching of pulp and paper and a method of preparation thereof is disclosed in WO 97/11164. WO 91/18974 describes a hemicellulase such as a glucanase, xylanase or mannanase active at an extreme pH and temperature. WO 94/25576 discloses an enzyme from *Aspergillus aculeatus*, CBS 101.43, exhibiting mannanase activity which may be useful for degradation or modification of plant or algae cell wall material. WO 93/24622 discloses a mannanase isolated from *Trichoderma reseei* useful for bleaching lignocellulosic pulps. An hemicellulase capable of degrading mannan-containing hemicellulose is described in WO91/18974 and a purified mannanase from *Bacillus amyloliquefaciens* is described in WO97/11164.

Preferably, the mannanase enzyme will be an alkaline mannanase as defined below, more preferably, a mannanase originating from a bacterial source. The terms "alkaline mannanase enzyme" is meant to encompass an enzyme having an enzymatic activity of at least 10%, preferably at least 25%, more preferably at least 40% of its maximum activity at a given pH ranging from 7 to 12, preferably 7.5 to 10.5.

Especially, the laundry detergent composition of the present invention will comprise an alkaline mannanase selected from the strain *Bacillus agaradhaerens* NICMB 40482; the mannanase from *Bacillus subtilis* strain 168 gene yght; the mannanase from *Bacillus sp.* I633 and/or the mannanase from *Bacillus sp.* AAI12. Most preferred mannanase for the inclusion in the detergent compositions of the present invention is the mannanase enzyme originating from *Bacillus sp.* I633 as described in the co-pending Danish patent application No PA 1998 01340.

The alkaline mannanase from *Bacillus agaradhaerens* NICMB 40482 is described in the co-pending U.S. patent application serial No. 09/111,256. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 32-343 of SEQ ID NO:2 as shown in U.S. patent application serial No. 09/111,256; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 97 to nucleotide 1029 as shown in U.S. patent application serial No. 09/111,256;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO 2 from amino acid residue 32 to amino acid residue 343 as shown in U.S patent application serial No. 09/111,256;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pSJ1678 comprising the polynucleotide molecule (the DNA sequence) encoding said mannanase has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Bucapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen

und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 18 May 1998 under the deposition number DSM 12180.

A second more preferred enzyme is the mannanase from the *Bacillus subtilis* strain 168, which is described in the co-pending U.S. patent application serial No. 09/095,163. More specifically, this mannanase is:

i) is encoded by the coding part of the DNA sequence shown in SED ID No. 5 shown in the U.S. patent application serial No. 09/095,163 or an analogue of said sequence; and/or

ii) a polypeptide comprising an amino acid sequence as shown SEQ ID NO:6 shown in the U.S. patent application serial No. 09/095,163; or

iii) an analogue of the polypeptide defined in ii) which is at least 70% homologous with said polypeptide, or is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed in the corresponding isolated polypeptide having mannanase activity selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO:5 as shown in the U.S. patent application serial No. 09/095,163

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 70% identical to the amino acid sequence of SEQ ID NO 6 as shown in the U.S. patent application serial No. 09/095,163;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

A third more preferred mannanase is described in the co-pending Danish patent application No. PA 1998 01340. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* I633;

ii) a polypeptide comprising an amino acid sequence as shown in positions 33-340 of SEQ ID NO:2 as shown in the Danish application No. PA 1998 01340; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of:

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 317 to nucleotide 1243 the Danish application No. PA 1998 01340;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO: 2 from amino acid residue 33 to amino acid residue 340 the Danish application No. PA 1998 01340;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM3 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH, Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 29 May 1998 under the deposition number DSM 12197.

A fourth more preferred mannanase is described in the Danish co-pending patent application No. PA 1998 01341. More specifically, this mannanase is:

i) a polypeptide produced by *Bacillus sp.* AAI 12;

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-362 of SEQ ID NO:2as shown in the Danish application No. PA 1998 01341; or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 65% homologous with said polypeptide, is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, or is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Also encompassed is the corresponding isolated polynucleotide molecule selected from the group consisting of

(a) polynucleotide molecules encoding a polypeptide having mannanase activity and comprising a sequence of nucleotides as shown in SEQ ID NO: 1 from nucleotide 225 to nucleotide 1236 as shown in the Danish application No. PA 1998 01341;

(b) species homologs of (a);

(c) polynucleotide molecules that encode a polypeptide having mannanase activity that is at least 65% identical to the amino acid sequence of SEQ ID NO 2 from amino acid residue 25 to amino acid residue 362 as shown in the Danish application No. PA 1998 01341;

(d) molecules complementary to (a), (b) or (c); and

(e) degenerate nucleotide sequences of (a), (b), (c) or (d).

The plasmid pBXM1 comprising the polynucleotide molecule (the DNA sequence) encoding a mannanase of the present invention has been transformed into a strain of the *Escherichia coli* which was deposited by the inventors according to the Budapest Treaty on the International Recognition of the Deposit of Microorganisms for the Purposes of Patent Procedure at the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH.

Mascheroder Weg 1b, D-38124 Braunschweig, Federal Republic of Germany, on 7 October 1998 under the deposition number DSM 12433.
The mannanase is incorporated into the detergent compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferred from 0.001% to 0.02% pure enzyme by weight of the composition.

The Pectate lyase enzyme

The second essential element of the detergent compositions of the present invention is a pectate lyase enzyme.

Pectate lyase is classified within the classification of enzymes provided by the Enzyme Nomenclature (1992) as EC 4.2.2.2. Said enzyme is known to split the α-1,4,glucoside bond of galacturonic acid found in pectin substances, creating a double bond between C4 and C5 and is subtantially free for other pectin degrading activities, i.e having less than 25%, preferably less than 15%, more preferably less than 5% by weight of the enzyme compound of other pectin degrading enzyme activities.

Pectate lyases have been cloned from different bacterial genera such as *Erwinia*, *Pseudomonas*, *Klebsiella* and *Xanthomonas*, *Streptomyces*, *Penicillium*, *Baceriodes*, *Thermomonospora*, *Fusarium*, *and Aspergillus*. Also from *Bacillus subtilis* (Nasser et al. (1993) FEBS **335**:319-326) and *Bacillus* sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. **58**:947-949) cloning of a pectate lyase has been described. Purification of pectate lyases with maximum activity in the pH range of 8-10 produced by *Bacillus pumilus* (Dave and Vaughn (1971) J Bacteriol. **108**:166-174), *B. polymyxa* (Nagel and Vaughn (1961) Arch. Biochem Biophys. **93**:344-352), *B. stearothermophilus* (Karbassi and Vaughn (1980) Can J. Microbiol. **26**:377-384), *Bacillus* sp. (Hasegawa and Nagel (1966) J. Food Sci

31:838-845) and *Bacillus* sp. RK9 (Kelly and Fogarty (1978) Can. J. Microbiol. 24:1164-1172) has been reported. WO 98/45393 discloses detergent compositions containing protopectinase with remarkable detergency against muddy soils.

Further suitable pectate lyases for use in the present invention are the protopectinases having an optimum reaction pH of 7.0 or higher when polygalacturonic acid is used as a substrate such as described in WO98/45393 and the pectic acid lyase having the amino acid sequence SEQ no 1 of EP 870 843 or having such amino acid sequence with one or more amino acid being deleted, added or substituted.

Preferred are the pectate lyase enzymes described in the international co-pending application PCT/DK98/00515, filed internationally on November 24, 1998 :

- A pectate lyase comprising a first amino acid sequence consisting of seven (7) amino acid residues having the following sequence: Asn Leu Asn Ser Arg Val Pro (NLNSRVP);
- A pectate lyase which is :

  i) a polypeptide produced by *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus agaradhaerens*, DSM 8721, of at least 99%, or

  ii) a polypeptide comprising an amino acid sequence as shown in positions 27-359 of SEQ ID NO:2 of PCT/DK98/00515, or

  iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

  iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or by a *Bacillus* species having a 16S rDNA sequence homology to *Bacillus licheniformis*, ATCC 14580, of at least 99%, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-341 of SEQ ID NO:4 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 233, and optionally also the arginine in position 238, is conserved and the derived polypeptide is at least 42% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form;

- A pectate lyase which is :

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:14 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:14 of PCT/DK98/00515 higher than 97.3%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 181-509 of SEQ ID NO:6 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) which is at least 50% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 390, and optionally also the arginine in position 395, is conserved and the derived polypeptide is at least 44% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is :

i) a polypeptide produced by the species *Bacillus halodurans*, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 42-348 of SEQ ID NO:8 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 240, and optionally also the arginine in position 245, is conserved and the derived polypeptide is at least 40% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form,

- A pectate lyase which is

i) a polypeptide produced by a *Bacillus* species having the 16S rDNA sequence of SEQ ID NO:13 of PCT/DK98/00515 or by a *Bacillus* species having a 16S rDNA sequence homology to SEQ ID NO:13 of PCT/DK98/00515 higher than 98.1%; or

ii) a polypeptide comprising an amino acid sequence as shown in positions 25-335 of SEQ ID NO:10 of PCT/DK98/00515, or

iii) an analogue of the polypeptide defined in i) or which is at least 45% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the arginine in position 227, and optionally also the arginine in position 232, is conserved and the derived polypeptide is at least 41% homologous with said polypeptide, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

Similarly preferred is the pectate lyase enzyme described in the international co-pending application PCT/DK98/00514, filed internationally on November 24, 1998 and which is :

i) a polypeptide produced by *Bacillus licheniformis*, ATCC 14580, or

ii) a polypeptide comprising an amino acid sequence as shown in positions 28-221 of SEQ ID NO:4 of PCT/DK98/00514, or

iii) an analogue of the polypeptide defined in i) or ii) which is at least 60% homologous with said polypeptide, or

iv) is derived from said polypeptide by substitution, deletion or addition of one or several amino acids, provided that the lysines in positions 133 and 155 and the arginine in position 158 are conserved and the derived polypeptide is at least 66% homologous with positions 60-158 of SEQ ID NO:4 of PCT/DK98/00514, or

v) is immunologically reactive with a polyclonal antibody raised against said polypeptide in purified form.

More preferred pectate lyases for the purpose of the present invention are those having opimum activity at pH's >7.0 and derived from Streptomyces fradiae Streptomyces nitrosporeus, Erwinia carotovora, Bacillus spheroides Thermomonospora fusca, Pseudomonas solanacearum, Bacteroides thetaiotaomicron, Fusarium solani, Xanthomonas campestris, Bacillus agaradhaerens, and/or Bacillus licheniformis.

Most preferred pectate lyase for the purpose of the present invention is the Pectate lyase from *Bacillus agaradhaerens*, NCIMB 40482 or DSM 8721.

The pectate lyase is incorporated into the compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferably from 0.001% to 0.02% pure enzyme by weight of the composition.

The Xyloglucanase enzyme

The third essential element of the present invention is a xyloglucanase enzyme such as described in the co-pending international patent application PCT/US98/09126, internationally filed by Procter and Gamble on May 5, 1998.

Suitable for the purpose of the present invention are these enzymes exhibiting endoglucanase activity specific for xyloglucan such that the catalytic turnover rate Kcat at the optimum conditions for the enzyme, is at least 5 times higher on xyloglucan than on carboxymethylcellulose.

As used herein, the term "endoglucanase activity" means the capability of the enzyme to hydrolyze 1,4-β-D-glycosidic linkages present in any xyloglucan material versus cellulose. The endoglucanase activity may be determined in accordance with methods known in the art, examples of which are described in WO 94/14953 and hereinafter. One unit of endoglucanase activity (e.g. CMCU AVIU, XGU or BGU) is defined as the production of 1 μmol reducing sugar/min from a glucan substrate, the glucan substrate being, e.g., CMC (CMCU) acid swollen Avicell (AVIU), xyloglucan (XGU) or cereal β-glucan (BGU) The reducing sugars are determined as described in WO 94/14953 and hereinafter The specific activity of an endoglucanase towards a substrate is defined as units/mg of protein.

Suitable are enzymes exhibiting high activity XGU endoglucanase activity (hereinafter "specific for xyloglucan"), which enzyme:

i) is encoded by a DNA sequence comprising or included in at least one of the following partial sequences

(a) ATTCATTTGT GGACAGTGGA C (SEQ ID No: 1)

(b) GTTGATCGCA CATTGAACCA (SEQ ID NO: 2)

(c) ACCCCAGCCG ACCGATTGTC (SEQ ID NO: 3)

(d) CTTCCTTACC TCACCATCAT (SEQ ID NO: 4)

(e) TTAACATCTT TTCACCATGA (SEQ ID NO: 5)

(f) AGCTTTCCCT TCTCTCCCTT (SEQ ID NO: 6)

(g) GCCACCCTGG CTTCCGCTGC CAGCCTCC (SEQ ID NO: 7)

(h) GACAGTAGCA ATCCAGCATT (SEQ ID NO: 8)

(i) AGCATCAGCC GCTTTGTACA (SEQ ID NO: 9)

(j) CCATGAAGTT CACCGTATTG (SEQ ID NO: 10)

(k) GCACTGCTTC TCTCCCAGGT (SEQ ID NO: 11)

(l) GTGGGCGGCC CCTCAGGCAA (SEQ ID NO: 12)

(m) ACGCTCCTCC AATTTTCTCT (SEQ ID NO: 13)

(n) GGCTGGTAG TAATGAGTCT (SEQ ID NO: 14)

(o) GGCGCAGAGT TTGGCCAGGC (SEQ ID NO: 15)

(p) CAACATCCCC GGTGTTCTGG G (SEQ ID NO: 16)

(q) AAAGATTCAT TTGTGGACAG TGGACGTTGA TCGCACATTG AACCAACCCC AGCCGACCGA
TTGTCCTTCC TTACCTCACC ATCATTTAAC ATCTTTTCAC CATGAAGCTT TCCCTTCTCT
CCCTTGCCAC CCTGGCTTCC GCTGCCAGCC TCCAGCGCCG
CACACTTCTG CGGTCAGTGG
GATACCGCCA CCGCCGGTGA CTTCACCCTG TACAACGACC
TTTGGGGCGA GACGGCCGGC
ACCGGCTCCC AGTGCACTGG AGTCGACTCC TACAGCGGCG
ACACCATCGC TTGTCACACC
AGCAGGTCCT GGTCGGAGTA GCAGCAGCGT CAAGAGCTAT GCCAACG
(SEQ ID NO:17) or

(r) CAGCATCTCC ATTGAGTAAT CACGTTGGTG TTCGGTGGCC
CGCCGTGTTG CGTGGCGGAG
GCTGCCGGGA GACGGGTGGG GATGGTGGTG GGAGAGAATG
TAGGGCGCCG TGTTTCAGTC

CCTAGGCAGG ATACCGGAAA ACCGTGTGGT AGGAGGTTTA TAGGTTTCCA GGAGACGCTG
TATAGGGGAT AAATGAGATT GAATGGTGGC CACACTCAAA CCAACCAGGT CCTGTACATA
CAATGCATAT ACCAATTATA CCTACCAAAA AAAAAAAAAA AAAAAAAAAA AAAA (SEQ ID NO:18)

or a sequence homologous thereto encoding a polypeptide specific for xyloglucan with endoglucanase activity,

ii) is immunologically reactive with an antibody raised against a highly purified endoglucanase encoded by the DNA sequence defined in i) and derived from *Aspergillus aculeatus*, CBS 101.43, and is specific for xyloglucan.

More specifically, as used herein the term "specific for xyloglucan" means that the endoglucanase enzyme exhibits its highest endoglucanase activity on a xyloglucan substrate, and preferably less than 75% activity, more preferably less than 50% activity, most preferably less than about 20% activity, on other cellulose-containing substrates such as carboxymethyl cellulose, cellulose, or other glucans.

Preferably, the specificity of an endoglucanase towards xyloglucan is further defined as a relative activity determined as the release of reducing sugars at optimal conditions obtained by incubation of the enzyme with xyloglucan and the other substrate to be tested, respectively. For instance, the specificity may be defined as the xyloglucan to β-glucan activity (XGU/BGU), xyloglucan to carboxy methyl cellulose activity (XGU/CMCU), or xyloglucan to acid swollen Avicell activity (XGU/AVIU), which is preferably greater than about 50, such as 75, 90 or 100.

The term "derived from" as used herein refers not only to an endoglucanase produced by strain CBS 101.43, but also an endoglucanase encoded by a DNA

sequence isolated from strain CBS 101.43 and produced in a host organism transformed with said DNA sequence. The term "homologue" as used herein indicates a polypeptide encoded by DNA which hybridizes to the same probe as the DNA coding for an endoglucanase enzyme specific for xyloglucan under certain specified conditions (such as presoaking in 5xSSC and prehybridizing for 1 h at ~40°C in a solution of 5xSSC, 5xDenhardt's solution, and 50 μg of denatured sonicated calf thymus DNA, followed by hybridization in the same solution supplemented with 50 μCi 32-P-dCTP labelled probe for 18 h at ~40°C and washing three times in 2xSSC, 0.2% SDS at 40°C for 30 minutes). More specifically, the term is intended to refer to a DNA sequence which is at least 70% homologous to any of the sequences shown above encoding an endoglucanase specific for xyloglucan, including at least 75%, at least 80%, at least 85%, at least 90% or even at least 95% with any of the sequences shown above. The term is intended to include modifications of any of the DNA sequences shown above, such as nucleotide substitutions which do not give rise to another amino acid sequence of the polypeptide encoded by the sequence, but which correspond to the codon usage of the host organism into which a DNA construct comprising any of the DNA sequences is introduced or nucleotide substitutions which do give rise to a different amino acid sequence and therefore possibly, a different amino acid sequence and therefore, possibly, a different protein structure which might give rise to an endoglucanase mutant with different properties than the native enzyme. Other examples of possible modifications are insertion of one or more nucleotides into the sequence, addition of one or more nucleotides at either end of the sequence, or deletion of one or more nucleotides at either end or within the sequence.

Endoglucanase specific for xyloglucan useful in the present invention preferably is one which has a XGU/BGU, XGU/CMU and/or XGU/AVIU ratio (as defined above) of more than 50, such as 75, 90 or 100.

Furthermore, the endoglucanase specific for xyloglucan is preferably substantially devoid of activity towards β-glucan and/or exhibits at the most 25% such as at the most 10% or about 5%, activity towards carboxymethyl cellulose and/or Avicell when the activity towards xyloglucan is 100%. In addition, endoglucanase specific for xyloglucan of the invention is preferably substantially devoid of transferase activity, an activity which has been observed for most endoglucanases specific for xyloglucan of plant origin.

Endoglucanase specific for xyloglucan may be obtained from the fungal species *A. aculeatus*, as described in WO 94/14953. Microbial endoglucanases specific for xyloglucan has also been described in WO 94/14953. Endoglucanases specific for xyloglucan from plants have been described, but these enzymes have transferase activity and therefore must be considered inferior to microbial endoglucanses specific for xyloglucan whenever extensive degradation of xyloglucan is desirable. An additional advantage of a microbial enzyme is that it, in general, may be produced in higher amounts in a microbial host, than enzymes of other origins.

The xyloglucanase of the invention may be isolated by a general method involving:

- cloning, in suitable vectors, a DNA library from *Aspergillus* spp.,
- transforming suitable yeast host cells with said vectors,
- culturing the host cells under suitable conditions to express any enzyme of interest encoded by a clone in the DNA library, and
- screening for positive clones by determining any endoglucanase activity of the enzyme produced by such clones.

A more detailed description of this screening method is given in WO 94/14953.

The DNA sequence coding for the enzyme may for instance be isolated by screening a cDNA library of *Aspergillus aculeatus*, e.g. strain CBS 101.43. publicly available from Centraalbureau voor Schimmelcultures, and selecting for

clones expressing enzymes having the ability to hydrolyze β-1,3 and/or β-1,4 bonds between two glucose molecules in polymers containing glucose (e.g. cellulose, cereal β-glucans or xyloglucans). The appropriate DNA sequence may then be isolated from the clone by standard procedures, e.g. as described in WO 94/14953, Example 1. It is expected that a DNA sequence coding for a homologous enzyme may be derived by similarly screening a cDNA library of another microorganism, in particular a fungus, such as a strain of *Aspergillus*, in particular *A. aculeatus* or *A. niger,* a strain of *Trichoderma*, in particular *T. harianun*, *T. reesie*, a strain of *Fusarium*, in particular *F. oxysporum* or a strain of *Humicola*.

Alternatively, the DNA coding for an endoglucanase of the invention may, in accordance with well-known procedures, conveniently be isolated from DNA from any of the above mentioned organisms by use of oligonucleotide probes, such as 20mer probes, prepared on the basis of a DNA sequence disclosed herein. For instance, a suitable oligonucleotide probe may, e.g., be prepared on the basis of any of the partial nucleotide sequences a)-p) listed in WO 94/14953.

The DNA sequence may subsequently be inserted into a recombinant expression vector. This may be any vector which may conveniently be subjected to recombinant DNA procedures, and the choice of vector will often depend on the host cell into which it is to be introduced. Thus, the vector may be an autonomously replicating vector, i.e. a vector which exists as an extrachromosomal entity, the replication of which is independent of chromosomal replication, e.g. a plasmid. Alternatively, the vector may be one which, when introduced into a host cell, is integrated into the host cell genome and replicated together with the chromosome(s) into which it has been integrated.

In the vector, the DNA sequence encoding the endoglucanase specific for xyloglucan should be operably connected to a suitable promoter and terminator sequence. The promoter may be any DNA sequence which shows transcriptional activity in the host cell of choice and may be derived from genes encoding proteins either homologous or heterologous to the host cell. The

procedures used to ligate the DNA sequences coding for the endoglucanase, the promoter and the terminator, respectively, and to insert them into suitable vectors are well known to persons skilled in the art (cf., for instance, Sambrook et al., Molecular Cloning. A Laboratory Manual, Cold Spring Harbor, NY 1989).

The host cell which is transformed with the DNA sequence encoding the enzyme useful for the present invention compositions is preferably a eukaryotic cell, in particular a fungal cell such as a yeast or filamentous fungal cell. In particular, the cell may belong to a species of *Aspergillus*, most preferably *Aspergillus oryzae* or *Aspergillus niger*. Fungal cells may be transformed by a process involving protoplast formation and transformation of the protoplasts followed by regeneration of the cell wall in a manner known in the art. The use of *Aspergillus* as a host microorganism is described in EP 238,023 (of Novo Nordisk A/S). The host cell may also be a yeast cell, e.g. a strain of *Saccharomyces*, in particular *Saccharomyces cerevisiae*.

The medium used to culture the transformed host cells may be any conventional medium suitable for growing the host cells in question. The expressed endoglucanase specific for xyloglucan may conveniently be secreted into the culture medium and may be recovered therefrom by well-known procedures including separating the cells from the medium by centrifugation or filtration. precipitating proteinaceous components of the medium by means of a salt such as ammonium sulphate, followed by chromatographic procedures such as ion exchange chromatography, affinity chromatography, or the like.

The thus purified endoglucanase may be employed for immunization of animals for the production of antibodies. More specifically, antiserum against the endoglucanase specific for xyloglucan may be raised by immunizing rabbits (or other rodents) according to the procedure described by N. Axelsen et al. in: A Manual of Quantitative Immunoelectrophoresis, Blackwell Scientific Publications. 1973, Chapter 23, or A. Johnstone and R. Thorpe, Immunochemistry in Practice. Blackwell Scientific Publications, 1982 (more specifically pp. 27-31). Purified immunoglobulins may be obtained from the antisera, for example by salt

precipitation ($(NH_4)_2SO_4$), followed by dialysis and ion exchange chromatography, e.g. on DEAE-Sephadex. Immunochemical characterization of proteins may be done either by Outcherlony double-diffusion analysis (O. Ouchterlony in: Handbook of Experimental Immunology (D.M. Weir, Ed.), Blackwell Scientific Publications, 1967, pp. 655-706), by crossed immunoelectrophoresis (N. Axelsen et al., supra, Chapters 3 and 4), or by rocket immunoelectrophoresis (N. Axelsen et al., Chapter 2).

The endoglucanases specific for xyloglucan useful in the present invention compositions may be produced essentially free from other plant cell wall degrading enzymes.

The enzyme preparation useful in the present invention compositions may be prepared in accordance with methods known in the art and may be in the form of a liquid or a dry preparation. For instance, the enzyme preparation may be in the form of a granulate or a microgranulate. The enzyme to be included in the preparation may also be stabilized in accordance with methods known in the art.

Test Methods:

Standard incubations: For characterization of enzymes, incubations are carried out in Eppendorf tubes comprising 1 ml of substrate (AZCL-xyloglucan substrates or pure polysaccharides from MegaZyme, Australia). 0.5ml 0.4% AZCL-substrate suspension is mixed with 0.5ml 0.1M citrate/phosphate buffer of optimal pH and 10 µl of a suitably diluted enzyme solution is added. Incubations are carried out in Eppendorf Theromixers for 15 minutes at 30°C (if not otherwise specified) before heat-inactivation for 20 minutes at 95°C. Enzyme incubations are carried out in triplicate. A blank is produced in which enzyme is added but inactivated immediately. After centrifugation the absorbance of the supernatant is measured in microtiter plates at 620nm and the blank is subtracted.

The activities of the enzymes are measured on different pure polysaccharides: xyloglucan and β-glucan from MegaZyme (AZCL-xyloglucan and AZCL-HE cellulose), CMC (Blanose from Aqualon) and Avicell (microcrystaline cellulose from Merck). Before use, Avicell is swelled in 85% orthophosphoric acid for 1 hour at room temperature and washed with acetone and water. 0.5% solutions/suspensions of the different substrates are made in 0.1M acetate buffer (if not otherwise specified) of the optimal pH, 10μl enzyme solutions are added to 1ml of substrate, incubations are carried at 30°C for 15 minutes before heat-inactivation as above. Reducing sugars are determined by reaction, in microtiter plates, with a PHBAH reagent comprising 0.15 g of para hydroxy benzoic acid hydrazide (Sigma H-9882), 0.50 g of potassium-sodium tartrate (Merck 8087) and 2% NaOH solution up to 10.0 ml. Results of blanks are subtracted. Glucose is used as a standard.

pH optimum is measured on substrates from MegaZyme (for the enzymes described hereinafter: EG II on AZCL-xylogulcan, EG III on pure β-glucan, and EG IV on AZCL-β-glucan). 0.5ml of 0.4% substrate is mixed with 0.5ml 0.1M citrate/phosphate buffer of varying pH and 10 μl of a suitably diluted enzyme solution is added. Incubations are carried out as described above. While enzymes useful herein may have optimum pH at any pH as desired to match the pH of the composition or cleaning method in which it will be used, preferably the enzymes useful herein are active within the pH range of from about pH 6-11, preferably 7-11, and more preferably within from about 8 to about 10.5.

The specificity of the different enzymes on the different AZCL-substrates is tested as above at optimal pH in 0.1M acetate buffer.

pH stability is measured by leaving the enzyme for 1 hour in 0.1 M citric acid/tri sodium phosphate buffers of varying pH before the enzyme is used for incubation of AZCL-β-glucan at the optimal pH.

Temperature optimum is measured by incubating the enzyme with AZCL-β-glucan substrate at varying temperatures for 15 minutes at the optimal pH.

Temperature stability is measured by leaving the enzyme, diluted in water, at various temperatures for 1 hour before incubation at 30°C with the relevant substrate.

Km and specific activity are measured by carrying out incubations at substrate concentrations (S) ranging from 0.025 to 1.5% (hereinafter: xyloglucan for EG II and β-glucan for EG IV), measure the reaction rate (v), picture S/v as a function of S, carry out linear regression analysis, finding the slope (=1/Vmax) and the intercept (Km/Vmax) and calculating Km and the specific activity (=Vmax/E), where E is the amount of enzyme added.

For gel filtration chromatography, 1% solutions/suspensions of the above mentioned pure polysaccharides are made. A suitable amount of enzyme is added and incubations are carried out for 0, 1, 2, 4 and 24 hours before heat-inactivation. 25µl of sample is injected into three TSK-columns in a row (PW G4000, PW G3000, PW G2500) and saccharides are eluted with 0.4M acetate buffer pH 3.0 at 0.8ml/min. Eluting saccharides are determined by a Shimadzu RI detector and data are collected and processed by Dionex software. Dextrans (from Sersa) are used as molecular weight standards.

Substrate specificity

The relative activity determined as the release of reducing sugar of different enzymes from different polysaccharides compared to the optimal substrate (100%) is provided in WO 94/14953 and reproduced in the table below.

Enzyme	EG II	EG III	EG IV
Avicell	1%	0%	3%
CMC	1%	2%	11%
β-glucan	0%	100%	100%
xyloglucan	100%	31%	0%

From these results the specificities of the different endoglucanases are presented as:

Enzyme	EG II	EG III	EG IV
XGU/BGU	∞	0.31	0
XGU/CMC	104	18	0
XGU/AVIU	114	∞	0
BGU/XGU	0	3.2	∞
BGU/CMC	0	58	9.4
BGU/AVIU	0	∞	25

The results of substrate specificity determined on AZCL-substrates is also provided in WO 94/14953, and reproduced in the following table:

Enzyme	EG II	EG III	EG IV
HE-cellulose	1%	100%	100%
β-glucan	0%	36%	56%
Xyloglucan	100%	33%	1%
Curdlan	0%	2%	4%

From the specificity results it is seen that compared to EG III and EG IV, EG II is specific for xyloglucan, as defined herein for use in the present invention compositions whereas the other two endoglucanases are not. EG III is active towards all types of substrates, but does not have its highest activity for xyloglucan, whereas EG IV cannot degrade xyloglucan and is very specific for β-glucans. (There are some differences in the results obtained with reducing sugars and AZCL-substrates. An explanation for this is that some AZCL substrates are more sensitive than others. In this case AZCL-HE-cellulose seems to be more sensitive than AZCL-β-glucan).

The Km and specific activity for EG II and EG III are provided in WO 94/14953. The standard deviations on 1/Vmax and Km/Vmax obtained from the linear regression analysis were used therein to calculate the intervals for the enzymes apparent from the following table:

Enzyme	Substrate	Km	Spec. act	r^2
		% Substrate	units/mg	
EG II	xyloglucan	0.242-0.306	106-119	0.98
EG III	β-glucan	0.136-0.207	165-186	0.98

Temperature optimum and temperature/pH stability - EG II and EG III have similar temperature optimums (optimal activity between 30°C and 60°C) and temperature stability (stable for 1h up to 60°C) but EG III is more stable at alkaline pH than EG II.

The gelfiltration chromatograms, which verify the substrate specificities, show that EG II degrades xyloglucan completely into oligomers of approximately 7-9 residues which are the known repeating subunits of xyloglucans (Fry, 1989). EG III degrades xyloglucan to a much lesser extent and EG IV does not degrade xyloglucan at all. EG III degrades β-glucan to a large extent into DP 3-4 and higher oligomers. This is in accordance with β-glucans being composed of 3-4 β-1, 4-linked glucose units in a row interrupted by single β-1, 3-linkages.

The xyloglucanase is incorporated into the detergent compositions of the invention preferably at a level of from 0.0001% to 2%, more preferably from 0.0005% to 0.1%, most preferably from 0.001% to 0.02% pure enzyme by weight of the composition.

Preferably, the detergent compositions of the present invention will comprise the three enzymes at the specific weight ratio of pure enzyme of mannanase to

pectate lyase to xyloglucananse of from 10:1:1 to 1:10:1 to 1:1:10. More preferably such ratio wil range from 5:1:1 to 1:5:1 to 1:1:5 and most preferably will be a 1:1:1 ratio.

The mannanase, pectate lyase and/or xyloglucanase enxcompassed in the detergent compositions of the present invention, in addition to the enzyme core comprising the catalytically domain, may also comprise a cellulose binding domain (CBD), the cellulose binding domain and enzyme core (the catalytically active domain) of the enzyme being operably linked. The cellulose binding domain (CBD) may exist as an integral part of the encoded enzyme, or a CBD from another origin may be introduced into the enzyme thus creating an enzyme hybrid. In this context, the term "cellulose-binding domain" is intended to be understood as defined by Peter Tomme et al. "Cellulose-Binding Domains: Classification and Properties" in "Enzymatic Degradation of Insoluble Carbohydrates", John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618, 1996. This definition classifies more than 120 cellulose- binding domains into 10 families (I-X), and demonstrates that CBDs are found in various enzymes such as cellulases, xylanases, mannanases. arabinofuranosidases, acetyl esterases and chitinases. CBDs have also been found in algae, e.g. the red alga Porphyra purpurea as a non-hydrolytic polysaccharide-binding protein, see Tomme et al., op.cit. However, most of the CBDs are from cellulases and xylanases, CBDs are found at the N and C termini of proteins or are internal. Enzyme hybrids are known in the art, see e.g. WO 90/00609 and WO 95/16782, and may be prepared by transforming into a host cell a DNA construct comprising at least a fragment of DNA encoding the cellulose- binding domain ligated, with or without a linker, to a DNA sequence encoding the mannanase and/or pectate lyase and/or xyloglucanase enzyme and growing the host cell to express the fused gene. Enzyme hybrids may be described by the following formula:

CBD - MR - X

wherein CBD is the N-terminal or the C-terminal region of an amino acid sequence corresponding to at least the cellulose binding domain; MR is the middle region (the linker), and may be a bond, or a short linking group preferably of from about 2 to about 100 carbon atoms, more preferably of from 2 to 40 carbon atoms; or is preferably from about 2 to to about 100 amino acids, more preferably of from 2 to 40 amino acids; and X is an N-terminal or C-terminal region of the mannanase, pectate lyase and/or xyloglucanase of the invention.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing metal binding sites to increase chelant stability.

Detergent components

The detergent compositions of the invention must contain at least one additional detergent component. The precise nature of these additional component, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

It has been further found that the performance of the detergent compositions of the present invention is enhanced by the addition of selected surfactants, a builder, another enzyme and/or a bleach system.

The detergent compositions according to the invention can be liquid, paste, gels, bars, tablets, spray, foam, powder or granular. Granular compositions can also be in "compact" form and the liquid compositions can also be in a "concentrated" form. Tablet compositions can be in single phase or multiple phase form.

In a first embodiment, the present invention relates to a laundry detergent and/or fabric care compositions comprising a mannanase, a pectate lyase and a xyloglucanase (Examples 1- 15). In a second embodiment, the present invention relates to dishwashing or household detergent compositions (Examples 16-24)

The compositions of the invention may for example, be formulated as hand dishwashing compositions, hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics and compositions for use in general household hard surface cleaning operations. When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components. Such compositions containing a pectate lyase, a mannanase and a xyloglucanase can provide fabric cleaning, stain removal, and color appearance when formulated as laundry detergent compositions.

When formulated as compositions suitable for use in a machine dish wash method, the compositions of the invention preferably contain a low foaming nonionic surfactant, a builder system, and one or more components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors.

The compositions of the invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process.

If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in

conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

Suitable detergent compounds for use herein are selected from the group consisting of the below described compounds.

Surfactant system

The detergent compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants. Preferably, the detergent compositions of the present invention will comprise a nonionic, an anionic and/or a cationic surfactant. Indeed, it has been surprisingly found that the detergent compositions of the present invention further comprising a nonionic, an anionic and/or a cationic surfactant, provide enhanced cleaning, i.e. superior stain removal, dingy cleaning and whiteness maintenance. Without wishing to be bound by theory, it is believed that the enzymatic hydrolysis of the combined three enzymes of the present invention, results in smaller particles being more easily removed by

nonionic surfactants known to focus on particulate soiling. Preferred nonionic surfactants are alkyl ethoxylated AE3 to AE7. It is also believed that the combination of the fabric substantive cationic surfactant with the enzymatic hydrolysis of the pectate lyase, mannanase and xyloglucanase provide improved performances.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of detergent compositions in accord with the invention.

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal^{TM} CO-630, marketed by the GAF Corporation; and Triton^{TM} X-

45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-3 (the condensation product of C_{12}-C_{13} linear alcohol with 3.0 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-5 (the condensation product of C_{14}-C_{15} linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, Kyro™ EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C_{12}-C_{14} alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)_t(\text{glycosyl})_x$$

wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6- position, preferably predominately the 2-position.

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Plurafac™ LF404 and Pluronic™ surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C_8-C_{14} alkyl phenol ethoxylates having from 3 to

ethoxy groups and C_8-C_{18} alcohol ethoxylates (preferably C_{10} avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.

```
R2 - C - N - Z,
     ||  |
     O   R1
```

wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or C_{16-18} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications comprise alkyl ester sulfonate surfactants of the structural formula :

```
                O
                ||
R3 - CH - C - OR4
      |
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SO_3M

wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is C_{10}-C_{16} alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is C_{10}-C_{16} alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a C_{10}-C_{24} hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C_{10}-C_{20} alkyl component, more preferably a C_{12}-C_{18} alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12}-C_{16} are preferred for lower wash temperatures (e.g. below about 50°C) and C_{16-18} alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for detersive purposes can also be included in the detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_8-C_{22} primary of secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline

earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8-C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C_{12}-C_{18} monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C_6-C_{12} diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k$-CH_2COO-M+ wherein R is a C_8-C_{22} alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO3M$ wherein R is an unsubstituted C_{10}-C_{24} alkyl or hydroxyalkyl group having a C_{10}-C_{24} alkyl component, preferably a C_{12}-C_{20} alkyl or hydroxyalkyl, more preferably C_{12}-C_{18} alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero

typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C_{12}-C_{18} alkyl polyethoxylate (1.0) sulfate (C_{12}-C_{18}E(1.0)M), C_{12}-C_{18} alkyl polyethoxylate (2.25) sulfate (C_{12}-C_{18}E(2.25)M), C_{12}-C_{18} alkyl polyethoxylate (3.0) sulfate (C_{12}-C_{18}E(3.0)M), and C_{12}-C_{18} alkyl polyethoxylate (4.0) sulfate (C_{12}-C_{18}E(4.0)M), wherein M is conveniently selected from sodium and potassium.

The detergent compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

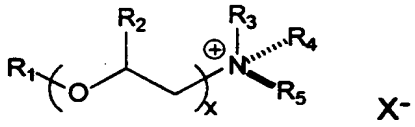
Cationic detersive surfactants suitable for use in the detergent compositions of the present invention are those having one long-chain hydrocarbyl group Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N+X-$$

wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups.

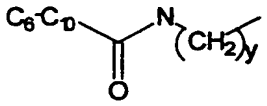
CH_2CHOH-$CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present invention has the formula (I):



Formula I

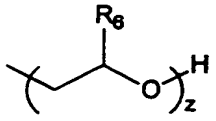
whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :



Formula II

y is 2-4, preferably 3.
whereby R2 is H or a C1-C3 alkyl,
whereby x is 0-4, preferably 0-2, most preferably 0,
whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,

whereby X^- is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R6 is C_1-C_4 and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby R_1 is C_8, C_{10} or mixtures thereof, x=o,
R_3, R_4 = CH_3 and R_5 = CH_2CH_2OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :

$$R_1R_2R_3R_4N^+X^- \text{ (i)}$$

wherein R_1 is C_8-C_{16} alkyl, each of R_2, R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_{40})_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2, R_3 or R_4 should be benzyl.
The preferred alkyl chain length for R_1 is C_{12}-C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.
Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :
coconut trimethyl ammonium chloride or bromide;
coconut methyl dihydroxyethyl ammonium chloride or bromide;
decyl triethyl ammonium chloride;
decyl dimethyl hydroxyethyl ammonium chloride or bromide;
C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
coconut dimethyl hydroxyethyl ammonium chloride or bromide;
myristyl trimethyl ammonium methyl sulphate;
lauryl dimethyl benzyl ammonium chloride or bromide;
lauryl dimethyl $(ethenoxy)_4$ ammonium chloride or bromide;

choline esters (compounds of formula (i) wherein R_1 is CH_2-CH_2-O-C-C_{12-14} alkyl and $R_2R_3R_4$ are methyl).

di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

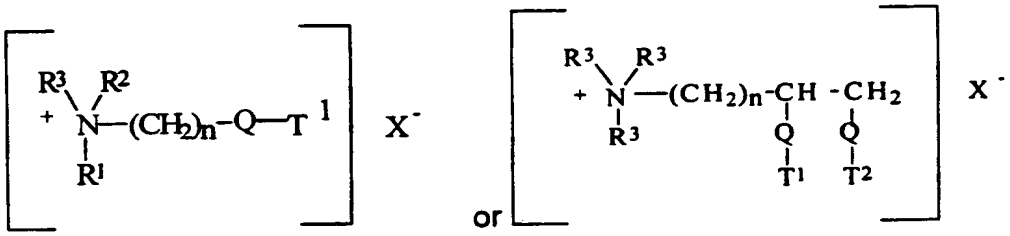
Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives or thei corresponding amine precursor, the most commonly used having been di-long alkyl chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

1) ditallow dimethylammonium chloride (DTDMAC);
2) dihydrogenated tallow dimethylammonium chloride;
3) dihydrogenated tallow dimethylammonium methylsulfate;
4) distearyl dimethylammonium chloride;
5) dioleyl dimethylammonium chloride;
6) dipalmityl hydroxyethyl methylammonium chloride;
7) stearyl benzyl dimethylammonium chloride;
8) tallow trimethylammonium chloride;
9) hydrogenated tallow trimethylammonium chloride;
10) C_{12-14} alkyl hydroxyethyl dimethylammonium chloride;
11) C_{12-18} alkyl dihydroxyethyl methylammonium chloride;
12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
13) di(tallow-oxy-ethyl) dimethylammonium chloride;
14) ditallow imidazolinium methylsulfate;
15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been presented as alternatives to the traditionally used di-long alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :



(I) (II)

wherein Q is selected from -O-C(O)-, -C(O)-O-, -O-C(O)-O-, $-NR^4-C(O)-$, $-C(O)-NR^4-$;

R^1 is $(CH_2)_n$-Q-T^2 or T^3;

R^2 is $(CH_2)_m$-Q-T^4 or T^5 or R^3;

R^3 is C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl or H;

R^4 is H or C_1-C_4 alkyl or C_1-C_4 hydroxyalkyl;

T^1, T^2, T^3, T^4, T^5 are independently C_{11}-C_{22} alkyl or alkenyl;

n and m are integers from 1 to 4; and

X^- is a softener-compatible anion. Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

The alkyl, or alkenyl, chain T^1, T^2, T^3, T^4, T^5 must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T^1, T^2, T^3, T^4, T^5 represents the mixture of long chain materials typical for tallow are particularly preferred.

Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;

2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;

3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;

4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;

5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;

6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;

7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl-ammonium chloride and

8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;

and mixtures of any of the above materials.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic

secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the detergent compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected

from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula

$$R^3(OR^4)xN(R^5)2 \rightarrow O$$

wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures therof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The detergent composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6-C_{12}, preferably C_6-C_{10} alkyl chain or $R_4X(CH_2)_n$. X is -O-,-C(O)NH- or -NH-, R_4 is a C_6-C_{12} alkyl chain n is between 1 to 5 preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines Suitable amines for use herein may be selected from 1-hexylamine. 1-

octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C8-C10 oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R1 and R2 are C_1-C_8 alkylchains or

$$-\left(CH_2-\underset{R_5}{CH}-O\right)_xH$$

R_3 is either a C_6-C_{12}, preferably C_6-C_{10} alkyl chain, or R_3 is $R_4X(CH_2)_n$, whereby X is -O-, -C(O)NH- or -NH-, R_4 is a C_4-C_{12}, n is between 1 to 5, preferably 2-3. R_5 is H or C_1-C_2 alkyl and x is between 1 to 6 .
R_3 and R_4 may be linear or branched ; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are $R_1R_2R_3N$ where R1 is a C6-C12 alkyl chain, R2 and R3 are C1-C3 alkyl or

$$-\left(CH_2-\underset{R_5}{CH}-O\right)_xH$$

where R5 is H or CH3 and x = 1-2.

Also preferred are the amidoamines of the formula:

$$R_1-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_n-N-(R_2)_2$$

wherein R_1 is C_6-C_{12} alkyl; n is 2-4,
preferably n is 3; R_2 and R_3 is C_1-C_4

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine,C8-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl

bis(hydroxyethyl)amine, coco bis(hydroxyehtyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated. lauryl amido propylamine and cocoamido propylamine.

Conventional detergent enzymes

Preferably, the detergent compositions can in addition to the mannanase, pectate lyase and xyloglucanase further comprise one or more enzymes which provide cleaning performance, fabric care and/or sanitisation benefits, preferably a protease, lipase, cellulase and/or amylase.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, other pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982

describes cellulases isolated from novel Bacillus species. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition

Peroxidase enzymes are used in combination with oxygen sources. e g percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching". i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International

Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substitued phenthiazine and phenoxasine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substitued syringates (C3-C5 substitued alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the

present invention. Also suitables are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE®, DURAZYM® and SAVINASE® from Novo and MAXATASE®, MAXACAL®, PROPERASE® and MAXAPEM® (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine protealytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is

described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128, +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04, 1997).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more

other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or ß) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α- and β-amylases. α-Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α-amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban® ,Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α-amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a

pH value in the range of 8 to 10, measured by the Phadebas® α-amylase activity assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimise their performance efficiency in the detergent compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively the variant may be designed such that the optimal pH, bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special atten-

must be paid to the cellulases as most of the cellulases have separate binding domains (CBD). Properties of such enzymes can be altered by modifications in these domains.

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cogranulates).

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Colour care and fabric care benefits

Technologies which provide a type of colour care benefit can also be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in copending European Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer (PCT/US97/16546) for colour care treatment and perfume substantivity are further examples of colour care / fabric care technologies and are described in the co-pending Patent Application No. 96870140.9, filed November 07, 1996.

Fabric softening agents can also be incorporated into detergent compositions in accordance with the present invention. These agents may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some

instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Bleaching agent

It has been surprisingly found that the detergent compositions of the present invention further comprising a bleaching agent, especially a bleach activator bleaching system, provide enhanced food stain removal and whiteness maintenance. Whithout wishing to be bound by theory, it is believed the smaller chromophoric particles resulting from the combined hydrolysis action of the pectate lyase, mannanase and xyloglucanase, are more easily attacked by the bleach activated system, especially at low temperature.

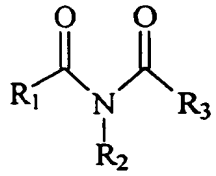
Preferred detergent ingredients that can be included in the detergent compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

The bleaching agent component for use herein can be any of the bleaching agents useful for detergent compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetylethylenediamine (TAED), nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3.5.-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG)or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in co-pending European Patent Application No. 91870207 7 and unsymetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R_1 is a C_7-C_{13} linear or branched chain saturated or unsaturated alkyl group, R_2 is a C_1-C_8, linear or branched chain saturated or unsaturated alkyl group and R_3 is a C_1-C_4 linear or branched chain saturated or unsaturated alkyl group.

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is bleached Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.

Builder system

The detergent compositions according to the present invention will preferably further comprise a builder system, more preferably an inorganic builder, most preferably Zeolite A, sodium layered silica and/or sodium tripolyphosphate. It has been surprisingly found that the detergent compositions of the present invention further comprising such builder, provide enhanced cleaning. Without wishing to be bound by theory, it is believed that the calcium deposit on pectin-and hydrocolloid gums containing stains/soil. Therefore, the use of the builder is believed to remove the entrapped calcium and favour the enzymatic action of the pectate lyase, mannanase and xyloglucanase.

Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene

phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($Na_2Si_2O_5$).

Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U S Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British

Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacar-boxylates and and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.
Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Other preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates

Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.
Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride.

such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates nitrilotriacetates, ethylenediamine tetraproprionates, triethylenetetraamine-hexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at lease low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alcanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil^{R}.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

Others

Other components used in detergent compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives. bactericides, tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials

comprise dextrins derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrins are,preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4" -bis-(2,4-dianilino-s-triazin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4-(N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-hydroxyethylamino)-s-triazin-6- ylami-no)stilbene-2,2'disulphonate, sodium 2(stilbyl-4"-(naphtho-1',2':4,5)-1,2,3 - triazole-2"-

sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners disclosed in EP 753 567.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula

$$(CH_3(PEG)_{43})_{0.75}(POH)_{0.25}[T\text{-}PO)_{2.8}(T\text{-}PEG)_{0.4}]T(PO\text{-}H)_{0.25}((PEG)_{43}CH_3)_{0.75}$$

where PEG is $-(OC_2H_4)O-$,PO is (OC_3H_6O) and T is $(pcOC_6H_4CO)$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol. the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups

However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3.000. The polyesters and their method of preparation are described in detail in EPA 311 342.

It is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein

Dispersants

The detergent composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.
Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the detergent compositions of the present invention.

The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of

sodium oleate in 30ml of water of 333ppm $CaCo_3$ (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C_{16}-C_{18} dimethyl amine oxide, C_{12}-C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12}-C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14}-C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Dye transfer inhibition

The detergent compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics

Polymeric dye transfer inhibiting agents

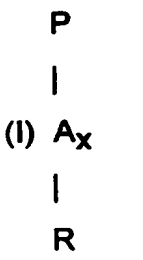
The detergent compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into detergent compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :



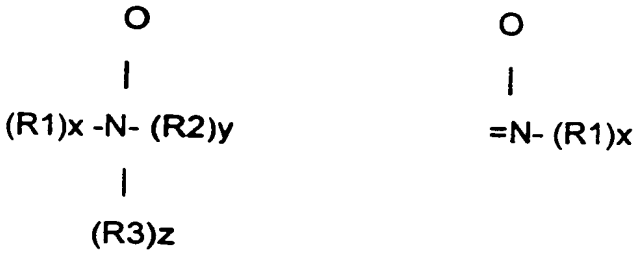
wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

|| || ||

A is NC, CO, C, -O-,-S-, -N- ; x is O or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general structures :



wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.
Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is part of said R group.
Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.
Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-0 functional group is attached to said R groups.
Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an

amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 2O,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113,"Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially vailable from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinyloxazolidone :

The detergent compositions of the present invention may also utilize polyvinyloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinyloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said

polyvinylimidazoles have an average about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

LAS	:	Sodium linear C_{11-13} alkyl benzene sulphonate.
TAS	:	Sodium tallow alkyl sulphate.
CxyAS	:	Sodium C_{1x} - C_{1y} alkyl sulfate.
CxySAS	:	Sodium C_{1x} - C_{1y} secondary (2,3) alkyl sulfate.
MBAS	:	Mid-branched alkyl sulfate.
CxyEz	:	C_{1x} - C_{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
CxyEzS	:	C_{1x} - C_{1y} sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
CxEOy	:	Cy alcohol with an average of ethoxylation of y.
Nonionic	:	Mixed ethoxylated/propoxylated fatty alcohol e.g. Plurafac LF404 being an alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
QAS	:	$R_2.N+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$-C_{14}.
SADS	:	Sodium C14-22 alkyl disulfate of the formula 2-R.C4H7 - 1,4-(SO4-)2 where R = C10-18.
MES	:	x-sulpho methyl ester of C18 fatty acid.
APA	:	C_{8-10} amido propyl dimethyl amine.
Soap	:	Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.

Neodol xy-z	:	C1x-C1y linear primary alcohol z ethoxylate.
CFAA	:	C_{12}-C_{14} alkyl N-methyl glucamide.
TFAA	:	C_{16}-C_{18} alkyl N-methyl glucamide.
TPKFA	:	C_{12}-C_{14} topped whole cut fatty acids.
DEQA	:	Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.
DEQA (2)	:	Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate.
DTDMAMS	:	Ditallow dimethyl ammonium methylsulfate.
SDASA	:	1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.
Silicate	:	Amorphous Sodium Silicate (SiO_2:Na_2O ratio = 1.6-3.2:1).
Metasilicate	:	Sodium metasilicate (SiO_2:Na_2O ratio = 1.0).
Zeolite A	:	Hydrated Sodium Aluminosilicate of formula $Na_{12}(AlO_2SiO_2)_{12}$. $27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
Na-SKS-6	:	Crystalline layered silicate of formula δ-$Na_2Si_2O_5$.
Citrate	:	Tri-sodium citrate dihydrate.
Citric	:	Anhydrous citric acid.
Borate	:	Sodium borate
Carbonate	:	Anhydrous sodium carbonate.
Bicarbonate	:	Sodium hydrogen carbonate.
Sulphate	:	Anhydrous sodium sulphate.
STPP	:	Sodium tripolyphosphate.
TSPP	:	Tetrasodium pyrophosphate.
MA/AA	:	Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	:	Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.

AA	:	Sodium polyacrylate polymer of average molecular weight 4,500.
Polycarboxylate	:	Copolymer comprising mixture of carboxylated monomers such as acrylate, maleate and methyacrylate with a MW ranging between 2,000-80,000 such as Sokolan commercially available from BASF, being a copolymer of acrylic acid, MW4,500.
PB1	:	Anhydrous sodium perborate monohydrate.
PB4	:	Sodium perborate tetrahydrate of nominal formula $NaBO_3.4H_2O$.
Percarbonate	:	Anhydrous sodium percarbonate of nominal formula 2.74 $Na_2CO_3.3H_2O_2$.
NaDCC	:	Sodium dichloroisocyanurate.
TAED	:	Tetraacetyl ethylene diamine.
NOBS	:	Nonanoyloxybenzene sulfonate in the form of the sodium salt.
NACA-OBS	:	(6-nonamidocaproyl) oxybenzene sulfonate.
DOBS	:	Decanoyl oxybenzene sulfonate in the form of the sodium salt.
DTPA	:	Diethylene triamine pentaacetic acid.
HEDP	:	1,1-hydroxyethane diphosphonic acid.
DETPMP	:	Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
EDDS	:	Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
Chelant	:	Chelant selected from EEDS, HEDP, DTPA, DETPMP and/or mixtures thereof.
MnTACN	:	Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.

Photoactivated Bleach	:	Sulfonated zinc phtalocyanine encapsulated in dextrin soluble polymer.
Photoactivated Bleach 1	:	Sulfonated alumino phtalocyanine encapsulated in dextrin soluble polymer.
PAAC	:	Pentaamine acetate cobalt(III) salt.
Paraffin	:	Paraffin oil sold under the tradename Winog 70 by Wintershall.
NaBz	:	Sodium benzoate.
Pectate lyase	:	Pectate lyase from *Bacillus agaradhaerens*, NCIMB 404482 or DSM 8721
Xyloglucanase	:	An endoglucanase specific for xyloglucan as described in co-pending patent application US serial No. SN60/045,826, filed May 5, 1997 and in WO 94/14953 as EG II.
Mannanase	:	Mannanase from *Bacillus agardhaerens*, NCIMB 40482
Protease	:	Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
Amylase	:	Amylolytic enzyme sold under the tradename Purafact Ox Am^R described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl®, Fungamyl® and Duramyl®. all available from Novo Nordisk A/S and those described in WO95/26397 (sold under the tradename Natalase By Novo Nordisk).
Lipase	:	Lipolytic enzyme sold under the tradename Lipolase Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.

Cellulase	:	Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
CMC	:	Sodium carboxymethyl cellulose.
PVNO	:	Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.
PVPVI	:	Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
Silicone antifoam	:	Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Suds Suppressor	:	12% Silicone/silica, 18% stearyl alcohol,70% starch in granular form.
Opacifier	:	Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
Thickener	:	High molecular weight crosslinked polyacrylates such as Carbopol offered by B.F. Goodrich Chemical Company and Polygel.
SRP 1	:	Anionically end capped poly esters.
SRP 2	:	Diethoxylated poly (1,2 propylene terephtalate) short block polymer.
QEA	:	bis($(C_2H_5O)(C_2H_4O)_n)(CH_3)$ -N^+-C_6H_{12}-N^+-(CH_3) bis((C_2H_5O)-$(C_2H_4O))_n$, wherein n = from 20 to 30
SCS	:	Sodium cumene sulphonate.
HMWPEO	:	High molecular weight polyethylene oxide.
PEGX	:	Polyethylene glycol,of a molecular weight of x.

PEO : Polyethylene oxide, with an average molecular weight of 5,000.

TEPAE : Tetreaethylenepentaamine ethoxylate.

BTA : Benzotriazole.

pH : Measured as a 1% solution in distilled water at 20°C.

Example 1

The following high density and bleach-containing laundry detergent compositions were prepared according to the present invention:

		I	II	III
Blown Powder				
	Zeolite A	12.0	-	15.0
	Sulfate	-	5.0	-
	LAS	3.0	-	3.0
	C45AS	3.0	2.0	4.0
	QAS	-	-	1.5
	DETPMP	0.4	0.4	0.4
	CMC	0.4	0.4	0.4
	MA/AA	1.0	2.0	2.0
Agglomerates				
	QAS	1.0	-	-
	LAS	-	11.0	7.0
	TAS	2.0	2.0	1.0
	Silicate	3.0	-	4.0
	Zeolite A	8.0	8.0	8.0
	Carbonate	8.0	8.0	4.0
Agglomerate				

		I	II	III
	NaSKS-6	15.0	12.0	5.0
	LAS	8.0	7.0	4.0
Spray On				
	Perfume	0.3	0.3	0.3
	C25E3	2.0	-	2.0
Dry additives				
	QEA	1.0	0.5	0.5
	Citric/Citrate	5.0	-	2.0
	Bicarbonate	-	3.0	-
	Carbonate	8.0	15.0	10.0
	TAED and/ or NACA-OBS	6.0	-	5.0
	NOBS	-	2.0	-
	Percarbonate/ PB1	14.0	7.0	10.0
	Polyethylene oxide of MW 5,000,000	-	-	0.2
	Bentonite clay	-	-	10.0
	Citric acid	4.0	-	1.5
	Pectate lyase	0.001	0.02	0.001
	Mannanase	0.005	0.002	0.001
	Xyloglucanase	0.001	0.002	0.001
	Protease	0.033	0.033	0.033
	Lipase	0.008	0.008	0.008
	Amylase	0.001	0.001	0.001
	Cellulase	0.0014	0.0014	0.0014
	Silicone antifoam	5.0	5.0	5.0
	Sulfate	-	3.0	-
Density (g/litre)		850	850	850

Moisture and miscellaneous	Up to 100%

Example 2

The following laundry compositions, which may be in the form of granules or tablet, were prepared according to the present invention.

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	18.0	11.0	-	10.0
SKS-6 (I) (dry add)	-	-	9.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0
Percarbonate	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-

	I	II	III	IV	V
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.004	0.004	0.008	0.007	0.01
Lipase	0.006	0.003	0.005	0.003	0.008
Amylase	0.003	0.015	0.007	0.006	0.010
Cellulase	0.001	0.0015	0.001	0.0014	0.003
Pectate lyase	0.001	0.005	0.001	0.05	0.005
Mannanase	0.005	0.001	0.001	0.005	0.005
Xyloglucanase	0.001	0.001	0.005	0.005	0.005
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1
Moisture and miscellaneous			Up to 100%		

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO4 / PVPVI/ Suds suppressor /PEG.

Example 3

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III
Agglomerate			
QAS	2.0	-	2.0
MES	-	2.0	-
LAS	6.0	-	-
TAS	-	2.0	-
C45AS	6.0	4.0	2.0
MBAS16.5, 1.9	4.0	-	-

		I	II	III
	Zeolite A	15.0	6.0	-
	Carbonate	4.0	8.0	4.0
	MA/AA	4.0	2.0	-
	CMC	0.5	0.5	-
	DETPMP	0.4	0.4	-
Spray On				
	C25E3	1.0	1.0	-
	Perfume	0.5	0.5	0.5
Agglomerate				
	SKS-6	7.0	15.0	20.0
	LAS	5.8	9.0	15.0
	Zeolite	-	0.9	-
	Water	0.08	0.1	-
Dry Adds				
	EDDS/HEDP	0.5	0.3	0.5
	NaSKS 6 (I)	5.0	6.0	4.0
	Citrate	-	1.0	-
	Citric	2.0	-	2.0
	NACA-OBS	4.1	-	5.0
	TAED	0.8	2.0	-
	Percarbonate	20.0	20.0	15.0
	SRP 1	0.3	0.3	-
	Pectate lyase	0.002	0.001	0.03
	Mannanase	0.002	0.010	0.003
	Xyloglucananse	0.020	0.001	0.003
	Protease	0.046	0.046	0.033
	Lipase	0.008	0.008	0.006
	Amylase	0.001	0.001	-
	QEA	1.0	-	1.0

	I	II	III
Silicone antifoam	1.0	0.5	0.5
Brightener 1	0.2	0.2	-
Brightener 2	0.2	-	0.2
Density (g/litre)	850	850	800
Moisture and miscellaneous		Up to 100%	

Example 4

The following laundry compositions, which may be in the form of granules or tablet, were prepared in accordance with the invention:

	I	II	III	IV	V
Base Product					
C45 AS/TAS	8.0	5.0	3.0	3.0	3.0
LAS	8.0	-	8.0	-	7.0
C25AE3S	0.5	2.0	1.0	-	-
LAS/NaSKS-6	5.0	17.0	9.0	20.0	15.0
C25AE5/AE3	2.0	-	5.0	2.0	2.0
QAS	-	-	-	1.0	1.0
Zeolite A	20.0	10.0	10.0	-	10.0
SKS-6	-	-	2.0	-	-
MA/AA	2.0	2.0	2.0	-	-
AA	-	-	-	-	4.0
Citrate	-	2.0	-	-	-
Citric	2.0	-	1.5	2.0	-
DTPA	0.2	0.2	-	-	-
EDDS	-	-	0.5	0.1	-
HEDP	-	-	0.2	0.1	-
PB1	3.0	5.0	10.0	-	4.0

	I	II	III	IV	V
PC	-	-	-	18.0	-
NOBS	3.0	4.0	-	-	4.0
NACA OBS	-	-	2.0	-	-
TAED	-	-	2.0	5.0	-
Carbonate	15.0	18.0	8.0	15.0	15.0
Sulphate	5.0	12.0	2.0	17.0	3.0
Silicate	-	1.0	-	-	8.0
Protease	0.004	0.004	0.008	0.007	0.01
Lipase	0.006	0.003	0.005	0.003	0.008
Amylase	0.003	0.015	0.007	0.006	0.010
Cellulase	0.001	0.0015	0.001	0.0014	0.003
Pectate lyase	0.001	0.010	0.003	0.001	0.03
Mannanase	0.005	0.002	0.003	0.001	0.03
Xyloglucanase	0.001	0.002	0.015	0.001	0.03
Minors	0.5	0.5	0.5	0.5	0.5
Perfume	0.2	0.3	0.5	0.2	0.1
Moisture and miscellaneous	Up to 100%				

Minors include Brightener / SRP1 / CMC / Photobleach / MgSO4 / PVPVI/ Suds suppressor /PEG.

Example 5

The following high density laundry detergent compositions were prepared according to the present invention:

	I	II	III	IV
Agglomerate				
QAS	2.0	-	2.0	-
MES	-	2.0	-	-
LAS	6.0	-	-	-

	I	II	III	IV
TAS	-	2.0	-	-
C45AS	6.0	4.0	2.0	-
MBAS16.5, 1.9	4.0	-	-	-
Zeolite A	15.0	6.0	-	-
Carbonate	4.0	8.0	4.0	8.0
MA/AA	4.0	2.0	-	2.0
CMC	0.5	0.5	-	0.5
DETPMP	0.4	0.4	-	0.5
Spray On				
C25E3	1.0	1.0	-	-
Perfume	0.5	0.5	0.5	0.5
Agglomerate				
SKS-6	7.0	15.0	20.0	10.0
LAS	5.8	9.0	15.0	10.0
Zeolite	-	0.9	-	-
C45 AS	-	3.0	-	-
Water	0.08	0.1	-	0.2
Dry Adds				
EDDS/HEDP	0.5	0.3	0.5	0.8
NaSKS 6)	5.0	6.0	4.0	11.0
Citrate	-	1.0	-	-
Citric	2.0	-	2.0	4.0
NAC OBS	4.1	-	5.0	4.0
TAED	0.8	2.0	-	2.0
Percarbonate	20.0	20.0	15.0	17.0
SRP 1	0.3	0.3	-	0.3
Pectate Lyase	0.005	0.001	0.004	0.030
Mannanase	0.005	0.010	0.004	0.003
Xyloglucanase	0.005	0.001	0.040	0.003

	I	II	III	IV
Protease	0.046	0.046	0.033	0.016
Lipase	0.008	0.008	0.006	-
Cellulase	0.0014	0.0014	0.001	0.001
Amylase	0.003	0.003	-	0.0015
QEA	1.0	-	1.0	1.0
Silicone antifoam	1.0	0.5	0.5	1.5
Brightener 1	0.2	0.2	-	6.2
Brightener 2	0.2	-	0.2	-
Density (g/litre)	850	850	800	775
Moisture and miscellaneous		Up to 100%		

Example 6

The following granular detergent were prepared in accordance with the present invention:

	I	II	III	IV
Base granule				
STPP	-	22.0	-	15.0
Zeolite A	30.0	-	24.0	5.0
Sulfate	5.5	5.0	7.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AE11S	-	1.0	-	1.0
MES	0.5	4.0	6.0	-
SADS	2.5	-	-	1.0

		I	II	III	IV
	Silicate	-	1.0	0.5	10.0
	Soap	-	2.0	-	-
	Brightener 1	0.2	0.2	0.2	0.2
	Carbonate	6.0	9.0	8.0	10.0
	PEG 4000	-	1.0	1.5	-
	DTPA	-	0.4	-	-
Spray on					
	C25E9	-	-	-	5.0
	C45E7	1.0	1.0	-	-
	C23E9	-	1.0	2.5	-
	Perfume	0.2	0.3	0.3	-
Dry additives					
	Carbonate	5.0	10.0	13.0	8.0
	PVPVI/PVNO	0.5	-	0.3	-
	Protease	0.033	0.033	0.033	0.0016
	Lipase	0.008	-	-	0.008
	Amylase	0.0016	-	-	0.0016
	Cellulase	0.0002	0.0005	0.0005	0.0002
	Pectate lyase	0.001	0.02	0.03	0.010
	Mannanase	0.005	0.002	0.003	0.001
	Xyloglucanase	0.001	0.002	0.008	0.001
	DTPA	0.5	0.3	0.5	1 0
	PB1	5	3.0	10	4 0
	NOBS/ TAED	0.5	0.3	0.5	0 6
	Sulfate	4.0	5.0	-	5 0
	SRP1	-	0.4	-	-
	Sud supressor	-	0.5	-	-
	speckle	0.9	-	2.7	1 2
Moisture and miscellaneous			Up to 100%		

Example 7

The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV	V	VI	VII
LAS	12.0	16.0	23.0	19	18.0	20.0	16.0
$C_{45}AS$		4.5	-		-	-	4.0
C_{45} E0.5S			-	-	-	-	-
C45 E3S	-	-	2.0	-	1.0	1.0	1.0
C45E6.5S	2.0	2.0	-	1.3	-	-	0.6
C_9-C_{14} alkyl dimethyl hydroxy ethyl quaternary ammonium salt			-	-	1.0	0.5	2.0
Tallow fatty acid			-	-	-	-	1.0
Tallow alcohol ethoxylate (50)	-	-	-	-	-	-	-
STPP	23.0	25.0	24.0	22,0	20.0	15.0	20 0
Carbonate	15.0	12.0	15.0	10.0	13.0	11.0	10 0
Sodium Polyacrylate (45%)	0.5	0.5	0.5	0.5	-	-	-
MA/AA	-	-	1.0	1.0	1.0	2.0	0 5
Silicate (1:6 ratio	3.0	6.0	9.0	8.0	9.0	6.0	8 0
Sulfate	25.0	18.0	20.0	18.0	20.0	22.0	13 0
PB1	5.0	5.0	10.0	8.0	3.0	1.0	2 0
PEG MW ~4000 (50%)	1.5	1.5	1.0	1.0	-	-	0 5
CMC	1.0	1.0	1.0	-	0.5	0.5	0 5

	I	II	III	IV	V	VI	VII
Citric	-	-	-	-	-	-	-
NOBS/ DOBS	0.5	1.0	0.5	0.5	1.0	0.7	0.3
TAED	1.5	1.0	2.5	3.0	0.3	0.2	0.5
SRP1	1.5	1.5	1.0	1.0	-	1.0	-
SRP2	-	-	-	-	1.0	-	1.0
Moisture	7.5	7.5	6.0	7.0	5.0	3.0	5.0
Mg sulphate	-	-	-	-	1.0	0.5	1.5
Chelant	-	-	-	-	0.8	0.6	1.0
Protease	0.004	0.004	0.008	0.007	0.01	0.015	0.015
Lipase	0.006	0.003	0.005	0.003	0.008	0.0014	0.0014
Amylase	0.003	0.015	0.007	0.006	0.010	0.002	0.0008
Cellulase	0.001	0.0015	0.001	0.0014	0.003	0.0001	0.0001
Pectate lyase	0.001	0.02	0.001	0.002	0.002	0.015	0.003
Mannanase	0.005	0.002	0.001	0.010	0.002	0.003	0.003
Xyloglucanase	0.001	0.002	0.008	0.002	0.02	0.003	0.003
speckle	2.5	4.1	4.2	4.4	5.6	5.0	5.2
Minors	1.0	1.0	1.0	1.0	0.5	1.5	1.0

Example 8

The following laundry detergent compositions were prepared in accordance with the present invention:

	I	II	III	IV
LAS	13.3	13.7	10.4	8.0
C_{45} AS	3.9	4.0	4.5	-
C_{45} E0.5S	2.0	2.0	-	-
C45 E3S	-	-	-	-
C45E6.5S	0.5	0.5	0.5	5.0

	I	II	III	IV
C_9-C_{14} alkyl dimethyl hydroxy ethyl quaternary ammonium salt	1.0	-	-	0.5
Tallow fatty acid	0.5	-	-	-
Tallow alcohol ethoxylate (50)	-	-	1.0	0.3
STPP	-	41.0	-	20.0
Zeolite A	26.3	-	21.3	1.0
Carbonate	23.9	12.4	25.2	17.0
Sodium Polyacrylate (45%)	3.4	0.0	2.7	-
MA/AA	-	-	1.0	1.5
Silicate (1:6 ratio)	2.4	6.4	2.1	6.0
Sulfate	10.5	10.9	8.2	15.0
PB1	1.0	1.0	1.0	2.0
PEG MW ~4000 (50%)	1.7	0.4	1.0	-
CMC	1.0	-	-	0.3
Citric	-	-	3.0	-
NOBS/ DOBS	0.2	0.5	0.5	0.1
TAED	0.6	0.5	0.4	0.3
SRP 1	1.5	-	-	-
SRP2	-	1.5	1.0	1.0
Moisture	7.5	3.1	6.1	7.3
Mn sulphate	-	-	-	1.0
Chelant	-	-	-	0.5
speckles	0.5	1.0	3.0	0.5
Pectate lyase	0.01	0.01	0.008	0.001
Mannanase	0.01	0.002	0.0008	0.01
Xyloglucanase	0.1	0.002	0.0008	0.001
Protease	0.004	0.004	0.008	0.007
Lipase	0.006	0.003	0.005	0.003
Amylase	0.003	0.015	0.007	0.006

	I	II	III	IV
Cellulase	0.001	0.0015	0.001	0.0014
Minors	1.0	1.0	1.0	1.0

Example 9

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	V
LAS	11.5	9.0	-	4.0	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	16.0	-
C23E9	-	3.0	2.0	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.0	-	3.0
TPKFA	2.0	-	2.0	0.5	2.0
Citric (50%)	6.5	1.0	2.5	4.0	2 5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0 05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	3 0
Na hydroxide	6.0	2.0	3.5	4.0	3 0
Ethanol	2.0	1.0	4.0	4.0	3 0
1,2 Propanediol	3.0	2.0	8.0	8.0	5 0
Monoethanolamine	3.0	1.5	1.0	2.5	1 0
TEPAE	2.0	-	1.0	1.0	1 0
Pectate lyase	0.05	0.001	0.005	0.045	0 008
Mannanase	0.005	0.001	0.050	0.045	0 008

	I	II	III	IV	V
Xyloglucanase	0.005	0.010	0.005	0.045	0.008
Protease	0.03	0.01	0.03	0.02	0.02
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	-	-	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Miscellaneous and water					

Example 10

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	IV	I	II	III	IV
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0

	I	II	III	IV	I	II	III	IV
Citric	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	0.4	0.3
TEPAE	0.5	-	0.5	0.2	2.0	1.2	1.0	-
DETPMP	1.0	1.0	0.5	1.0				
Pectate lyase	0.001	.001	.001	0.003	0.003	.002	.002	0.005
Mannanase	0.001	.001	0.005	0.003	0.030	.002	.002	0.005
Xyloglucanase	0.001	0.01	.001	0.030	0.003	0.002	0.010	.005
Protease	0.02	0.02	0.01	.008	-	-	.003	.003
Lipase	-	.002	-	.002	.004	0.01	0.01	0.01
Amylase	.004	.004	0.01	.008	-	-	.004	.003
Cellulase	-	-	-	.002	-	-	0.004	0.002
SRP 2	0.3	-	0.3	0.1	1.0	1.5	2.5	2 5
Boric acid	0.1	0.2	1.0	2.0	4.0	4.0	-	-
Ca chloride	-	0.02	-	0.01	0.1	0.2	0.3	-
Brightener 1	-	0.4	-	-	0.4	-	-	-
Suds suppressor	0.1	0.3	-	0.1	0.8	0.7	-	-
Opacifier	0.5	0.4	-	0.3	8.0	7.5	8.0	8 2
NaOH up to pH	8.0	8.0	7.6	7.7				
Miscellaneous and water								

Example 11

The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts by weight, enzyme are expressed in pure enzyme) :

	I	II
LAS	28.0	19.0
C45AS	14.0	6.0
C13E8	3.0	3.0
Oleic acid	3.0	2.5
Citric	5.0	5.0
Na hydroxide	0.4	4.0
Ca Formate	0.2	0.1
Na Formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	6.0	5.5
Xylene sulfonic acid	-	2.0
TEPAE	1.5	0.8
Protease	0.05	0.02
Pectate lyase	0.005	0.01
Mannanase	0.005	0.01
Xyloglucananse	0.005	0.01
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume	0.5	0.3
Water and Minors		

Example 12

The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

	I	II
C45AS	-	10.0
LAS	7.6	-
C68AS	1.3	-
C45E7	4.0	-
C25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Pectate lyase	0.043	0.001
Mannanase	0.043	0.01
Xyloglucanase	0.043	0.001
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-

	I	II
Silicate	3.0	5.0
Carbonate	10.0	10.0
Suds suppressor	1.0	4.0
CMC	0.2	0.1
Miscellaneous and minors	Up to 100%	

Example 13

The following rinse added fabric softener composition was prepared according to the present invention :

DEQA (2)	20.0
Pectate lyase	0.001
Mannanase	0.001
Xyloglucanase	0.001
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
$CaCl_2$	0.20
Perfume	0.90
Miscellaneous and water	Up to 100%

Example 14

The following fabric softener and dryer added fabric conditioner compositions were prepared according to the present invention :

	I	II	III	IV	V

	I	II	III	IV	V
DEQA	2.6	19.0	-	-	-
DEQA(2)	-	-	-	-	52.0
DTMAMS	-	-	-	26.0	-
SDASA	-	-	70.0	42.0	40.2
Stearic acid of IV=0	0.3	-	-	-	-
Neodol 45-13	-	-	13.0	-	-
HCL	0.02	0.02	-	-	-
Ethanol	-	-	1.0	-	-
Pectate lyase	0.005	0.002	0.001	0.01	0.002
Mannanase	0.05	0.002	0.001	0.01	0.002
Xyloglucanase	0.05	0.002	0.001	0.01	0.002
Perfume	0.3	1.0	0.75	1.0	1.5
Glycoperse S-20	-	-	-	-	15.4
Glycerol monostearate	-	-	-	26.0	-
Digeranyl Succinate	-	-	0.38	-	-
Silicone antifoam	0.01	0.01	-	-	-
Electrolyte	-	0.1	-	-	-
Clay	-	-	-	3.0	-
Dye	10ppm	25ppm	0.01	-	-
Water and minors	100%	100%	-	-	-

Example 15

The following laundry bar detergent compositions were prepared according to the present invention (Levels are given in parts per weight, enzyme are expressed in pure enzyme) :

	I	II	III	VI	V	III	VI	V
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Pectate lyase	0.01	0.001	0.005	0.001	0.02	0.004	0.001	.0005
Mannanase	0.001	0.001	.0005	0.001	0.002	0.004	0.001	.0005
Xyloglucanase	0.001	0.001	.0005	0.001	0.002	0.004	0.005	0.005
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	-	.0003	-	-	.0003	.0002	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3

	I	II	III	VI	V	III	VI	V
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

Example 16

The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	-	51.0	51.0	-	-	44.3
Citrate	17.0	-	-	50.0	40.2	-
Carbonate	17.5	14.0	20.0	-	8.0	33.6
Bicarbonate	-	-	-	26.0	-	-
Silicate	15.0	15.0	8.0	-	25.0	3.6
Metasilicate	2.5	4.5	4.5	-	-	-
PB1	10.0	8.0	8.0	-	-	-
PB4	-	-	-	10.0	-	-
Percarbonate	-	-	-	-	11.8	4.8
Nonionic	2.0	1.5	1.5	3.0	1.9	5.9
TAED	2.0	-	-	4.0	-	1.4
HEDP	1.0	-	-	-	-	-
DETPMP	0.6	-	-	-	-	-
MnTACN	-	-	-	-	0.01	-
PAAC	-	0.01	0.01	-	-	-
Paraffin	0.5	0.4	0.4	0.6	-	-
Pectate lyase	0.01	0.002	0.03	0.05	0.005	0.005

	I	II	III	IV	V	VI
Mannanase	0.001	0.002	0.003	0.005	0.005	0.001
Xyloglucanase	0.01	0.002	0.003	0.005	0.005	0.001
Protease	0.072	0.053	0.053	0.026	0.059	0.01
Amylase	0.012	0.012	0.012	0.021	0.021	0.006
Lipase	-	0.001	-	0.005	-	-
BTA	0.3	0.2	0.2	0.3	0.3	0.3
Polycarboxylate	6.0	-	-	-	4.0	0.9
Perfume	0.2	0.1	0.1	0.2	0.2	0.2
pH	11.0	11.0	11.3	9.6	10.8	10.9
Miscellaneous, sulfate and water				Up to 100%		

Example 17

The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention :

	I	II	III	IV	V	VI
STPP	30.0	33.5	27.9	29.6	33.8	22.0
Carbonate	30.5	30.5	30.5	23.0	34.5	45.0
Silicate	7.0	7.5	12.6	13.3	3.2	6.2
Metasilicate	-	4.5	-	-	-	-
Percarbonate	-	-	-	-	4.0	-
PB1	4.4	4.5	4.3	-	-	-
NADCC	-	-	-	2.0	-	0.9
Nonionic	1.0	0.7	1.0	1.9	0.7	0.5
TAED	1.0	-	-	-	0.9	-
PAAC	-	0.004	-	-	-	-
Paraffin	0.25	0.25	-	-	-	-
Pectate lyase	0.01	0.005	0.002	0.002	0.02	0.001

	I	II	III	IV	V	VI
Mannanase	0.01	0.005	0.02	0.002	0.02	0.001
Xyloglucnanase	0.01	0.005	0.002	0.02	0.02	0.005
Protease	0.036	0.021	0.03	-	0.006	-
Amylase	0.03	0.005	0.004	-	0.005	-
Lipase	0.005	-	0.001	-	-	-
BTA	0.15	0.15	-	-	0.2	-
Perfume	0.2	0.2	0.05	0.1	0.2	-
pH	10.8	11.3	11.0	10.7	11.5	10.9
Miscellaneous, sulfate and water	Up to 100%					

Example 18

The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm^2 using a standard 12 head rotary press

	I	II	III	IV	V	VI	VII	VIII
STPP	-	48.8	54.7	38.2	-	52.4	56.1	36 0
Citrate	20.0	-	-	-	35.9	-	-	-
Carbonate	20.0	5.0	14.0	15.4	8.0	23.0	20.0	28 0
Silicate	15.0	14.8	15.0	12.6	23.4	2.9	4.3	4 2
Pectate lyase	0.01	0.002	0.02	0.001	0.002	0.033	0.02	0 02
Mannanase	0.001	0.002	0.002	0.001	0.02	0.033	0.02	0 02
Xyloglucanase	0.001	0.002	0.02	0.001	0.002	0.033	0.02	0 02
Protease	0.042	0.072	0.042	0.031	0.052	0.023	0.023	0 029
Amylase	0.012	0.012	0.012	0.007	0.015	0.003	0.017	0 002
Lipase	0.005	-	-	-	-	-	-	-
PB1	14.3	7.8	11.7	12.2	-	-	6.7	8 5
PB4	-	-	-	-	22.8	-	3.4	-

	I	II	III	IV	V	VI	VII	VIII
Percarbonate	-	-	-	-	-	10.4	-	-
Nonionic	1.5	2.0	2.0	2.2	1.0	4.2	4.0	6.5
PAAC	-	-	0.02	0.009	-	-	-	-
MnTACN	-	-	-	-	0.007	-	-	-
TAED	2.7	2.4	-	-	-	2.1	0.7	1.6
HEDP	1.0	-	-	0.9	-	0.4	0.2	-
DETPMP	0.7	-	-	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.5	-	-	0.5	-
BTA	0.2	0.3	0.3	0.3	0.3	0.3	0.3	-
Polycarboxylate	4.0	-	-	-	4.9	0.6	0.8	-
PEG	-	-	-	-	-	2.0	-	2.0
Glycerol	-	-	-	-	-	0.4	-	0.5
Perfume	-	-	-	0.05	0.2	0.2	0.2	0.2
Weight of tablet	20g	25g	20g	30g	18g	20g	25g	24g
pH	10.7	10.6	10.7	10.7	10.9	11.2	11.0	10.8
Miscellaneous, sulfate and water	Up to 100%							

Example 19

The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	I	II	III	IV
STPP	17.5	17.2	23.2	23.1
Carbonate	-	2.4	-	-
Silicate	6.1	24.9	30.7	22.4
NaOCl	1.1	1.1	1.1	1.2
Thickener	1.0	1.1	1.1	1.0
Nonionic	-	0.1	0.06	0.1

	I	II	III	IV
NaBz	0.7	-	-	-
Pectate lyase	0.005	0.001	0.001	0.002
Mannanase	0.001	0.001	0.005	0.002
Xyloglucanase	0.001	0.005	0.001	0.002
NaOH	1.9	-	-	-
KOH	3.6	3.0	-	-
Perfume	0.05	-	-	-
pH	11.7	10.9	10.8	11.0
Water	up to 100%			

Example 20

The following liquid rinse aid compositions were prepared according to the present invention :

	I	II	III	IV
Mannanase	0.001	0.001	0.005	0.005
Xyloglucanase	0.01	0.001	0.001	0.001
Pectate lyase	0.001	0.001	0.001	0.001
Nonionic	10.0	13.6	62.3	60.0
Propylene glycol	-	-	5.0	5.5
Citric	3.5	4.6	-	-
SCS	10.0	7.7	-	-
pH of the liquid	3.0	2.5	7.2	7.2
Miscellaneous, solvent and water	Up to 100%			

Example 21

The following manual liquid dishwashing compositions were prepared according to the present invention :

	I	II	III	IV	V	VI	VII
C12-14E06-2S	25.0	28.0	26.0	30.0	20.0	26.0	26.0
C12-14 alkyl dimethyl amine oxide	2.0	6.0	6.0	7.8	5.0	6.0	6.0
C12-14 alkyl dimethyl betaine	2.0	-	-	-	-	-	-
C12-14 glucose amide	3.0	1.0	-	-	-	-	-
C11EO9	-	1.0	-	4.0	2.0	-	-
C9-11EO8	5.0	-	3.0	-	-	3.0	3.0
DTPA	-	0.1	-	-	-	-	-
SCS	-	1.0	3.5	3.0	2.5	3.5	3.5
Xylene sulfonate	-	3.0	-	-	-	-	-
Mg hydroxide	1.0	-	-	-	-	-	-
Mg chloride	0.4	2.6	-	-	-	-	-
1,3 bis (methylamino) cyclohexane	-	-	0.7	1.0	0.3	2.5	0.7
N,N-dimethylamino) ethyl methacrylate homopolymer	-	-	0.2	0.5	0.2	0.2	0 2
Citric	-	-	3.0	-	-	-	-
Maleic acid	-	-	-	2.5	-	-	-
Ethanol	8.0	5.0	7.0	7.0	4.0	7.0	7 0
Protease	-	-	-	-	-	-	0 02
Amylase	-	-	-	-	-	0.005	-
Pectate lyase	0.005	0.002	0.005	0.001	0.005	0.01	0.001
Mannanase	0.001	0.02	0.005	0.001	0.005	0.01	0 01
Xyloglucanase	0.001	0.002	0.05	0.002	0.005	0.01	0.001

	I	II	III	IV	V	VI	VII
Perfume	0.2	0.5	0.5	0.4	0.3	0.5	0.5
Water and minors	Up to 100%						

Example 22

The following liquid hard surface cleaning compositions were prepared according to the present invention :

	I	II	III	IV	V
Pectate lyase	0.005	0.01	0.03	0.02	0.008
Mannanase	0.001	0.01	0.03	0.002	0.008
Xyloglucanase	0.001	0.01	0.03	0.002	0.008
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12,13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Neodol 23-3	-	-	-	-	1.5
Neodol 91-10	-	-	-	-	1.6

	I	II	III	IV	V
C25AE1.8S	-	-	-	6.0	
Na paraffin sulphonate	-	-	-	6.0	
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	
Ethoxylated tetraethylene pentaimine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water			Up to 100%		

*Na4 ethylenediamine diacetic acid

**Diethylene glycol monohexyl ether

Example 23

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

Pectate lyase	0.01
Mannanase	0.01
Xyloglucananase	0.01
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8

Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%

*Diethylene glycol monobutyl ether

Example 24

The following disinfecting compositions were prepared according to the present invention.

	I Wipe	II Spray	III Liquid
H2O2	1.0	1.5	1.0
Na tetraborate 10.H2O	-	1.0	-
C10 Amine Oxide	-	0.9	0.9
C12-14 alkyl dimethyl amine oxide	0.4	-	-
C7-10 AS	-	-	6.0
C9-11EO10	-	0.05	-
C8-18 Fatty acid	-	0.1	0.2
Ethanol	9.0	1.0	2.5
Benzyl alcohol	-	0.8	-
Propylene or diethylene glycol butyl ether	1.0	1.5	-
Poly(propylene glycol) monobutyl ether	0.2	-	-
HEDP	-	0.1	-
Butylated hydroxytoluene	0.01	0.06	0.03
Salicyclic acid	0.03	-	0.07
Pectate lyase	0.001	0.01	0.005
Mannanase	0.001	0.01	0.001
Xyloglucanase	0.002	0.01	0.001

	I	II	III
Perfume	0.1	0.3	0.3
Citric	0.7	-	1.5
Dye	-	-	2.0
NaOH	-	0.1	-
Miscellaneous and water	Up to 100%		

CLAIMS

1. A detergent composition comprising a detergent ingredient, a mannanase enzyme, a pectate lyase enzyme and a xyloglucanase enzyme.

2. A detergent composition according to claim 1 wherein said mannanase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.02% pure enzyme by weight of total composition.

3. A detergent composition according to claims 1-2 wherein said pectate lyase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of total composition.

4. A detergent composition according to claims 1-3 wherein said xyloglucanase is present at a level of from 0.0001% to 2%, preferably from 0.0005% to 0.5%, more preferably from 0.001% to 0.1% pure enzyme by weight of total composition.

5. A detergent composition according to claims 1-4 wherein said enzymes are present at a weight ratio of pure enzymes of mannanase to pectate lyase to xyloglucanase of from 10:1:1 to 1:10:1 to 1:1:10, preferably of from 5:1:1 to 1:5:1 to 1:1:5 and more preferably is 1:1:1.

6. A detergent composition according to any of the preceding claims wherein said detergent ingredient is selected from anionic, nonionic, cationic surfactant, and/or mixtures thereof.

7. A detergent composition according to any of the preceding claims wherein said detergent ingredient is a bleaching agent, preferably a bleach activator bleaching system.

8. A detergent composition according to any of the preceding claims wherein said detergent ingredient is a builder, preferably selected from zeolite A, sodium layered silicate, sodium tripolyphosphate and/or mixtures thereof.

9. A detergent composition according to any of the preceding claims wherein said detergent ingredient is an enzyme, preferably selected from lipase, protease, amylase and or cellulase and/or mixtures thereof.

10. Method of cleaning a fabric, a dishware and/or a hard surface with detergent composition according to any of the preceding claims.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00791

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 98 39403 A (THE PROCTER & GAMBLE CO.) 11 September 1998 (1998-09-11)	1,6-10
A	page 6, line 25 - line 36 page 28, line 24 - page 29, line 2 claims 1,6,9-11; examples 19,20	2-5

E	WO 99 02663 A (NOVO NORDISK A/S) 21 January 1999 (1999-01-21) page 7, line 35 - page 8, line 6 page 19 - page 36	1,6-10

X	WO 95 35362 A (GIST BROCADES BV) 28 December 1995 (1995-12-28) cited in the application claims 1-17 page 5, line 30 - page 6, line 4	1

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 September 1999	20/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/00791

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 98 06808 A (THE PROCTER & GAMBLE CO.) 19 February 1998 (1998-02-19) cited in the application claims 1-3,5-7,12-14; example 19 page 4 - page 6 page 9 - page 18	1,3,6-10
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WO 9850513 A	12-11-1998	NONE	